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BENZO (A) PYRENE AND TRACE METALS IN CHARLESTON, SOUTH CAROLINA

Carl Spangler, et al

Environmental Protection Agency
Research Triangle Park, North Carolina

June 1975

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

Charleston, S. C., along with some other cities in the Southeastern Coast and Gulf Coast area, has an anomalously high incidence of deaths resulting from lung cancer - about 50 percent higher than the national average. Benzo[a]pyrene (BaP) and trace metals are widely suspected of being causative agents in lung cancer. A survey of BaP and trace metals in the ambient air in Charleston reveals, however, that the air concentrations are lower than the national averages, generally falling in the 0.01 to 29 percentile among American cities.

To test the view that atmospheric concentrations of BaP can readily be inferred from soil concentrations, soil samples were taken in Charleston at sites roughly corresponding to the area in which air was subject to testing in the air sampling program. There are few values from the United States with which to compare the Charleston soil values, though the soil concentrations of BaP there are somewhat higher than observed urban values in the Soviet Union, for example. Accordingly, from the limited data available, the Charleston soil values of BaP do not appear extraordinarily high.

Thus, it seems safe to infer that the abnormally high death rate resulting from lung cancer is not due to higher-than-normal exposure to the agents addressed.

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PREFACE

Carl Spangler, who was a trace metal specialist for the Environmental Protection Agency, initiated the sampling reported here to see if a correlation could be established between trace metal and benzo[a]pyrene concentrations and lung cancer mortality. Mr. Spangler's untimely death in November 1972 occurred just as the results of the sampling program were beginning to come in. In December 1973, Mr. Spangler's colleagues in EPA commissioned Noel de Nevers of the University of Utah, who had spent a year at EPA and worked with Mr. Spangler, to write this report, summarizing and analyzing the results of the sampling program.

CONTENTS

Page

LIST OF FIGURES vi

LIST OF TABLES vii

ABSTRACT viii

INTRODUCTION 1

SAMPLING PROGRAM 3

EXPERIMENTAL RESULTS 4
ANALYSIS OF AIR SAMPLING DATA 7
ANALYSIS OF SOIL SAMPLING FOR BaP - CHARLESTON, S.C. 10
ANALYSIS OF SOIL SAMPLING FOR BaP - WEST VIRGINIA 12

ANALYTICAL RELIABILITY 14

HISTORICAL PROBLEM 15

CONCLUSIONS 16

REFERENCES 17

APPENDIX A. STUDY OF BaP, Be, Cd, Cr, Cu, AND Ni IN AIR AT CHARLESTON, S.C., NOVEMBER 1972 THROUGH MARCH 1973 19

APPENDIX B. ANALYSIS OF BENZO[a]PYRENE IN SOIL SAMPLES 39

LIST OF FIGURES

Figure		Page
1	Observed BaP Concentrations (ppm) in Soil, in Charleston, S.C. (Values Represent Highest Concentration Measured at Site from Table 2.)	11
A-1	Outline Map of Charleston, S.C., Showing Locations of Air Sampling Sites	21
A-2	Weekly Average BaP Content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973.	24
A-3	Weekly Average Be content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	24
A-4	Weekly Average Cd Content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973.	25
A-5	Weekly Average Cr Content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	25
A-6	Weekly Average Cu Content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	26
A-7	Weekly Average Ni Content of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	26
A-8	Average Weekly Temperatures at Charleston, S.C., from November 1, 1972, to March 31, 1973	27
A-9	Wind Roses for Days During which BaP Content of Air was Relatively High at Sampling Stations.	29
A-10	Wind Roses for Days During which Be Content of Air was Relatively High at Sampling Stations.	30
A-11	Wind Roses for Days During which Cd Content of Air was Relatively High at Sampling Stations	31
A-12	Wind Roses for Days During which Cr Content of Air was Relatively High at Sampling Sites	32
A-13	Wind Roses for Days During which Cu Content of Air was Relatively High at Sampling Stations	33
A-14	Wind Roses for Days During which Ni Content of Air was Relatively High at Sampling Stations	34

LIST OF TABLES

Table		Page
1	Summary of Measurements of Trace Constituents in Ambient Air at Charleston, S.C., November 1, 1972, through March 31, 1973	4
2	Analysis of BaP Content of Soil In and Around Charleston, S.C.	5
3	Analysis of BaP Content of Soil Samples from Coal Refuse Banks in West Virginia - Kentucky	7
4	Comparison of Charleston, S.C., Ambient Air Trace Constitutent Values with National Values	10
5	Summary of Reported Soil Concentrations of BaP	13
A-1	Average Airborne Concentrations of BaP and Five Metals at Charleston, November 1, 1972, to March 31, 1973	22
A-2	Range of Values for Selected Air Pollutants During Winter Months at Charleston and Selected Mid-Atlantic Cities	22
A-3	Relative Air Pollution Levels at Three Sampling Stations in Charleston, November 1, 1972, to March 31, 1973	23
A-4	Wind Direction Observations Recorded at Hi-Vol Air Sampling Sites and at Charleston Municipal Airport	28
A-5	Possible Source Directions for Air Pollutants at Three Hi-Vol Air Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	35
A-6	Weekly Average BaP and Metal Contents of Air at Three Sampling Sites in Charleston, S.C., November 1, 1972, to March 31, 1973	37
B-1	Results of Sample Analysis for Soils Taken in West Virginia (Coal Refuse Banks) and in Charleston, S.C.	45

ABSTRACT

Charleston, S.C., along with some other cities in the Southeastern Coast and Gulf Coast area, has an anomalously high incidence of deaths resulting from lung cancer - about 50 percent higher than the national average. Benzo[a]pyrene (BaP) and trace metals are widely suspected of being causative agents in lung cancer. A survey of BaP and trace metals in the ambient air in Charleston reveals, however, that the air concentrations are lower than the national averages, generally falling in the 0.01 to 29 percentile among American cities.

To test the view that atmospheric concentrations of BaP can readily be inferred from soil concentrations, soil samples were taken in Charleston at sites roughly corresponding to the area in which air was subject to testing in the air sampling program. There are few values from the United States with which to compare the Charleston soil values, though the soil concentrations of BaP there are somewhat higher than observed urban values in the Soviet Union, for example. Accordingly, from the limited data available, the Charleston soil values of BaP do not appear extraordinarily high.

Thus, it seems safe to infer that the abnormally high death rate resulting from lung cancer is not due to higher-than-normal exposure to the agents addressed.

In addition to the testing mentioned, because of the suspected high emission rate of BaP from burning coal refuse banks, a group of samples were taken in the vicinity of several refuse banks in West Virginia. Data from the analyses show that soils there do not contain abnormally high amounts of BaP.

BENZO[a]PYRENE AND TRACE METALS IN CHARLESTON, SOUTH CAROLINA

INTRODUCTION

Considerable, and apparently uncontroverted, evidence[1] shows that the incidence of death from lung cancer (defined as malignant neoplasm of the bronchus, trachea, and lung) is not uniform across the United States, but rather is significantly higher than average in the Southeastern Coast and the Gulf Coast area. In the most recent survey available (1959-1961), the national average death rate from lung cancer for white males per 100,000 of population was 40.79. The cities with the highest death rates for white males from this cause were:

City	Annual death rate for white males per 100,000 population (1959-1961)
Lake Charles, La.	62.31
Albany, Ga.	61.34
Charleston, S. C.	60.63
New Orleans, La.	59.74
Shreveport, La.	55.90
Galveston, Texas	55.88
Jersey City, N. J.	55.87

Jersey City, in seventh place, is the first city to appear on the list that is not part of the "Southeastern Coast and Gulf Coast area." This anomaly in the incidence of death from lung cancer has not been satisfactorily explained. An epidemiological study[2] of the Charleston area suggests that airborne particulate matter in the city itself is a possible cause of this anomaly, at least for that locality. Similarily, medical evidence has been adduced[3,4] to suggest that generally, if not in these cities, trace metals and benzo[a]pyrene (BaP) are implicated in the causation of lung cancer.

This background impelled the late Carl Spangler, who was trace-metal specialist for the National Air Data Branch of the Environmental Protection Agency (EPA), to initiate a sampling program to see if a correlation could be established between trace metal and BaP concentrations and lung cancer mortality. Charleston was chosen as the sampling site because it was close to Mr. Spangler's office in Durham, N.C., was high on the lung cancer mortality list, and had a public health department that was interested in the effects of air pollution and willing to cooperate in the program.

Mr. Spangler's untimely death in November 1972 occurred just as the results of the sampling program were beginning to come in; thus, he had no part in the analysis of the data. In December 1973, Mr. Spangler's colleagues in EPA commissioned Noel de Nevers of the University of Utah, who had spent a year at EPA and worked with Mr. Spangler, to write this report summarizing and analyzing the results of the sampling program. Chemical analysis was conducted under EPA contract by Geological Resources, Inc., Raleigh, N.C., and by the Research Triangle Institute, Research Triangle Park, N.C.

SAMPLING PROGRAM

The program consisted of two parts: air sampling and soil sampling. The air sampling was conducted at three sites chosen to represent (1) suburban air far from major industry, (2) air in a downtown commercial district, and (3) air directly across the river from the industrial district of Charleston. At each site filters from Hi-Vol samplers were regularly collected for the period November 1, 1972, to March 31, 1973. The filters were collected by the Charleston County Health Department and sent directly to Geological Resources, Inc., for analysis. Samples from the filters were analyzed for BaP, beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), and nickel (Ni). The test methods and results are detailed in Appendix A.

The soil sampling program was initiated largely as a result of the extensive work by Shabad[5] who showed that the concentration of BaP in soils bears a strong relationship to proximity of suspected sources of BaP emissions and, hence, presumably is an indicator of the average atmospheric BaP concentration in the air over that particular section of soil. If it can be established that one can reliably infer pollutant concentrations in air from concentrations in soil, it will then be possible to make detailed surveys of airborne pollutant levels and concentration gradients using soil sampling techniques, which are more rapid and less expensive than air sampling methods.

This relationship has not yet been convincingly demonstrated. To test it, soil samples roughly corresponding to the area whose air would be tested by the air sampling program mentioned above were taken in Charleston. In addition, because of the suspected high emission rate of BaP from burning coal refuse banks[6], a group of samples were taken in the vicinity of several refuse banks in West Virginia. These samples were subjected to the same analytical procedure as the results from Charleston. The analytical procedures used and the concentrations found are detailed in Appendix B and in Reference 7.

EXPERIMENTAL RESULTS

The experimental results of the sampling program are shown in Table 1, which summarizes the air sampling results; Table 2, which summarizes the soil sampling results from Charleston; and Table 3, which summarizes the soil sampling results from the burning coal refuse bank areas in West Virginia.

ANALYSIS OF AIR SAMPLING DATA

The significance of the Charleston data in Table 1 is most apparent when compared with pollutant values in other urban areas. In the following analysis, particular

Table 1. SUMMARY OF MEASUREMENTS OF TRACE CONSTITUENTS IN AMBIENT AIR AT CHARLESTON, S. C., NOVEMBER 1, 1972, THROUGH MARCH 31, 1973
All results in nanograms/m^3 (1 nanogram = 10^{-9} g = 10^{-3} microgram)

Location	BaP	Be	Cd	Cr	Cu	Ni
Radio Station WTMA (22 samples)						
Minimum	0.0028	0	0.1267	0.0916	16.0	0.1466
Maximum	1.2409	0.1609	0.8232	2.1474	155.3	2.4883
Average	0.5711	0.0373	0.2751	0.7293	62.9	0.8332
Queen St. Fire Station (22 samples)						
Minimum	0.1693	0	0.1590	0.0797	8.9	0.2610
Maximum	1.6787	0.1247	0.6328	1.3573	253.4	1.6172
Average	0.7441	0.0287	0.3024	0.5870	59.0	0.8306
Mt. Pleasant Post Office (22 samples)						
Minimum	0.1995	0	0.1136	0	11.4	Trace
Maximum	1.9767	0.1529	0.9245	0.9413	139.8	1.5188
Average	0.7448	0.0363	0.2531	0.3589	47.2	0.6359
Total (66 samples)						
Minimum	0.0028	0	0.1136	0	8.9	Trace
Maximum	1.9767	0.1609	0.9245	2.1474	253.4	2.4883
Average	0.6866	0.0341	0.2768	0.5584	56.4	0.7666

Table 2. ANALYSIS OF BaP CONTENT OF SOIL IN AND AROUND CHARLESTON, S.C.

Location (EPA sample no.)	Reported BaP concentration, ppm	
	by RTI[a]	by GR[b]
100 yds south of U.S. Army-Charleston Depot, Hydrocarbon storage, 100 yds east of N. Rhett Rd. (C-19A-A)	0.216	2.1007
50 yds east of Virginia Ave., 0.25 mile west of West Virginia Co. Pulp Mill. (C-19C1-A)	1.920	1.0569
100 yds east of Virginia Ave. in small public park adjacent to major hydrocarbon storage areas. (C-26A-A)	3.634	4.6451
St. Johns and McMillin Aves., 100 yds from all traffic. Vacant section outside Naval Hospital area. (C-25C)	1.003	-
Chicora and English Sts., outside fence of U.S. Navy "fuel farm." (C-32B)	-	4.0113
Back of Esso Tank Storage on Greenleaf St. about 300 yds from Cooper River. (C-39O)	-	3.6893
About 0.5 mile north of Airco Ferroalloys plant along gravel access road and railroad switches. (C-39B-A)	0.150	3.1108
Near Columbus and Immigration Sts., near Port Authority docks, 200 yds from highway. (C-46D-A)	33.528	5.4251
Cleared block, 100 yds west of Concord St., 100 yds south of Laurens St. (C-53B-A)	3.520	5.4859
Vacant lot at Limehouse St. and Murray Blvd. (C-52D)	-	2.4673
Cleared city block (center) Barr, Wentworth, Halsey, and Beaufain Sts. (C-52B)	27.709	-
Residential area at Third Ave. and Wagener St. (C-45B)	1.095	-
Ashepoo Lane, 50 yds west of I-26, 100 yds south of Koppers, 100 yds in front of Agrico Chemical. (C-39A1-A)	0.953	2.8488
Vacant industry site, 50 yds north of Koppers storage, 200 yds west of I-26, elevated, on Col. Nitrogen Road. (C-39A2-A)	97.612	18.3454

Table 2 (continued). ANALYSIS OF BaP CONTENT OF SOIL IN AND AROUND CHARLESTON, S. C.

Location (EPA sample no.)	Reported BaP concentration, ppm	
	by RTI[a]	by GR[b]
100 yds from Hagood oil-fired power plant, 60 yds north of Col. Nitrogen. (C-39A(3)-A)	1.875	2.0669
0.5 mile northeast of Mobile Chemical, alongside old, unused plant entrance road next to swamp. (C-32C)	-	1.18787
Wilbur St., in industrial park, opposite Bird and Sons. (C-31A)	0.606	-
Corner lot at Firestone and Blossom Sts. 2 miles from south end of airport runway. (C-24A)	0.696	-
Corner lot at Prince and Taylor Sts. 0.5 mile from south end of airport runway. (C17B-A)	-	4.2829
Ashley-Phosphate Road, 1.25 mile from north end of airport runway. (C-3A)	-	7.1528
Carteret and Vassar Sts., vacant lot in high economic level residential area. (C-38A-A)	2.502	6.3879
Burning Tree and Greentree Lane, vacant lot in residential area. (C52C-A)	0.231	4.1038
Riverside Beach Road, rural. (C-47D-A)	0.489	3.6123
20 yds beyond end of Moultrie St. in residential area; space heating with oil heater is common. (C-62A-A)	0.255	4.2925
Residential area at end of Flynn Street at Ashley River. (C-23-B)	-	1.3308

[a]Research Triangle Institute (RTI) reports considerable variation in results depending on method used.[8] The highest value is reported here.

[b]Geological Resources (GR).

emphasis will be given to comparison of the Charleston survey data with the nationwide data reported in Air Quality Data for Organics, 1969 and 1970[8] and Air Quality Data for Metals, 1968 and 1969,[9] both of which are EPA compilations.

Consider first the results for BaP. The averages at the three sampling locations in Charleston were 0.57, 0.74, and 0.74 nanograms per cubic meter (ng/m^3). For

Table 3. ANALYSIS OF BaP CONTENT OF SOIL SAMPLES FROM COAL REFUSE BANKS IN WEST VIRGINIA - KENTUCKY

Location (EPA sample no.)	Reported BaP concentration, ppm	
	by RTI[a]	by GR[b]
Cedar Grove, W. Va.[c]		
25 ft. from upper south edge of culm bank, from steep hillside; necessary to separate gravel and roots. (A-1-A)	1.004	5.451
60 ft. from bank, uphill (60° slope). (A-2-A)	0.076	2.383
100 ft. from bank, uphill. (A-3-A)	0.432	3.200
1/8 mile from bank, below stripped area. All from undisturbed soil, washed-over spots avoided. (A-4-A-)	0.326	3.851
Hand-selected yellowish platy crystals (with some coal) from bank blow hole edges at surface. Other holes flaming in high wind, nearby small sample. (A-5)	-	26.043 (6.051)[d]
Marnie, W. Va.[e]		
Control sample taken at small hillside cemetary, approximately 1 mile south of bank. 100 yds. from highway. (A-6)	0.513	-
50 yds. from bank between railroad and cliff. (A-7)	1.475	-
50 yds. from bank between railroad and cliff, and about 100 yds. from previous sample. (A-8)	0.969	-
Taken between stream and highway and 100 yds. from previous sample. (A-9)	22.200	-
Huntington-Ashland area[f]		
Taken in residential area, 0.5 mile downhill from end of west runway of Ashland-Huntington Airport. (B-1)	-	1.600
Taken 300 yds., same elevation, from end of runway. (B-2)	-	1.452
Taken at Neal, W. Va., in field adjacent to gas compressor station and across Big Sandy River from Ashland Refinery, West. (B-3)	-	3.707
0.5 mile south of Ashland Refinery on Kentucky side of Big Sandy River. (B-4)	-	2.184
75 yds. west of center of Ashland Refinery, midway from each of two main units, which were about 0.25 mile away. (B-5)	-	4.261
Taken just outside of fenceline, about 200 yds. from Semet Solvay coke ovens at Ashland, Kentucky. (B-6)	-	2.501
Taken across railroad and highway in open field, about 0.5 mile southwest from Semet Solvay coke ovens. (B-7)	-	4.529
Taken in Riverside Community, near bank of Ohio River, about 2 miles south of Semet Solvay coke ovens. (B-8)	-	4.725

[a]Research Triangle Institute (RTI) reports considerable variation in results depending on method used. The highest value is reported here.

[b]Geological Resources, Inc. (GR).

[c]Samples obtained on May 31, 1972--a cloudy, windy day with temperature of 55°F; rain occurred the previous day.

[d]Duplicate sample.

[e]Samples obtained on June 1, 1972--a windy, partly cloudy day with temperature of 60°F. Samples were taken in and around a single burning coal refuse bank.

[f]Samples obtained in the Huntington, W. Va., and Ashland, Ky., area on June 1, 1972--a windy partly cloudy day with temperature of 60°F.

1970, annual averages are available for 164 cities[8]; these values ranged from a high of 3.09 to a low of 0.30 ng/m^3. On a percentile basis, if the average of the three Charleston sampling stations is used, then the resultant average of 0.68 ng/m^3 corresponds to the 14th percentile of the range of American cities. Stated another way, 14 percent of the typical American cities listed will have lower concentrations than Charleston and 86 percent will have higher concentrations than Charleston. Moreover, this comparison somewhat overstates the concentration in Charleston because it compares values taken in winter in Charleston with annual averages for the other cities. Typically, concentrations of BaP are higher in winter because of seasonally greater emissions from space heating. The maximum value measured in Charleston (1.97 ng/m^3) corresponds to the 66th percentile of the observed annual averages; i.e., 34 percent of American cities have annual average concentrations higher than the maximum measured value in Charleston.

It can be concluded from this comparison that in terms of BaP concentrations in the air, Charleston is in the cleanest 20 percent of American cities. Other cities having 1970 BaP annual averages close to the winter average measured in Charleston are Little Rock, Arkansas; Riverside, San Diego, and San Francisco, California; Des Moines, Iowa; Guayanilla, Puerto Rico; and Burlington, Vermont. None of these cities are centers of heavy industry or of major coal burning sources of BaP.

For trace metals, the evidence supports the same conclusion, namely that Charleston has ambient air concentrations that are lower than national averages, but the form of the available data makes it difficult to state the result as precisely as for BaP. The reason for the difficulty is that many or all of the results reported by EPA are reported as "below the limits of detection" or zero. For example, of the 736 reported values for beryllium (Be) in 1969, all but 9 were reported as zeros. From the data in Reference 9, it seems clear that any value less than 0.1 ng/m^3 for Be was reported as a zero. The averages at all sites in Charleston were about 0.03 ng/m^3, so that if they were included in this tabulation they would also be reported as zero. Thus, for Be there seems to be little to be said, other than that the values obtained were not large enough to attract interest.

For the other four metals surveyed (Cd, Cr, Cu, and Ni), however, most of the values reported are non-zero. For cadmium, EPA[9] reported annual averages in 1969 for 183 cities. The reported values ranged from 3 to 105 ng/m^3. All values less than 3 ng/m^3 were reported as zeros; there were 26 such values. The measured average at Charleston (Table 1) is 0.3 ng/m^3; in the tabulation by EPA, it would be reported

as a zero. Thus it can be said that measurements place Charleston in the lowest 13 percent of American cities in ambient Cd levels. However, because the value in Charleston is only one-tenth of that which is the lowest reported by EPA, the value in Charleston must correspond to a percentile much lower than 13 percent. If the 1969 values are plotted on log-normal paper, they form a reasonably straight line over the range of 3 to 38 ng/m^3. If extrapolated to the 0.3 ng/m^3 average measured at Charleston, it corresponds to the 0.01 percentile; i.e., only 1 out of 10,000 American cities would be expected to have cadmium concentrations this low. This extrapolation is not certain; so the result should not be taken too literally; but it does show that the measured values of cadmium in Charleston are extremely low.

Survey findings for chromium follow a pattern similar to the cadmium result. EPA[9] has tabulated 1969 annual average Cr values for 184 cities. These values ranged from 7 to 102 ng/m^3. All values less than 7 ng/m^3 were reported as zeros; there were 110 such values. The measured Cr value in Charleston averaged 0.5 ng/m^3, which is less than one-tenth of the detectable limit reported by EPA.[9] Thus, the results in Charleston must be in the lower 60 percent (110/184 = 60 percent) of the sample of American cities. If the 1969 annual average values (7 to 102 ng/m^3) are plotted on log-normal paper, they make a reasonably straight line. If extrapolated to the average Cr value found in Charleston, it corresponds to about the second percentile; i.e., 98 percent of American cities would be expected to have higher chromium concentrations than Charleston.

For copper, which is more abundant in the air than the other metals sampled, the problem of zero values does not exist; the 184 annual average values for 1969 reported in by EPA[9] ranged from 20 to 1280 ng/m^3 with no zeros. The measured average in Charleston was 56 ng/m^3, which corresponds to the 29th percentile; 71 percent of American cities would, therefore, have higher ambient Cu concentrations than Charleston.

Finally, EPA[9] reported 1969 annual average values for nickel for 183 cities; these ranged from 7 to 173 ng/m^3. All values less than 7 ng/m^3 were reported as zeros; 46 of the 183 average values (25 percent) fall in this category. The measured average value in Charleston was 0.7 ng/m^3, about one-tenth of the detectable limit reported by EPA. Based on the results of the two surveys, Charleston would rank in the lower 25 percent of American cities in ambient nickel concentrations. Moreover, if the reported values are plotted on log-normal paper and extrapolated to the observed value in Charleston, Charleston is placed at about the 0.02 percentile; i.e., only 2 out of 10,000 American cities would be expected to have nickel concentrations this low.

From these results (summarized in Table 4), it can be concluded that with respect to the trace constitutents studied, Charleston is one of the cleanest cities in the United States for which sample data are available.

Table 4. COMPARISON OF CHARLESTON, S.C. AMBIENT AIR TRACE CONSTITUTENT VALUES WITH NATIONAL VALUES

Constitutent	Average measured winter season value in Charleston, S.C. (Winter 1972-1973), ng/m^3	Corresponding percentile of American urban areas (annual average 1970[a]
Benzo[a]pyrene	0.68	14
Beryllium	0.034	-
Cadmium	0.28	0.01
Chromium	0.55	2
Copper	56	29
Nickel	0.77	0.02

[a]Some data are for 1969.

ANALYSIS OF SOIL SAMPLING FOR BaP - CHARLESTON, S.C.

Figure 1 is a map of the Charleston area with values in parts-per-million (ppm) resulting from the analysis of BaP in soil (Table 2) placed at the location where the sample was taken.[7] If the two laboratories that conducted soil analyses found conflicting results, the larger of the two reported values was plotted.

The values shown on Figure 1 may be grouped as follows:

0.6 to 7 ppm - 22 values

27 to 97 ppm - 3 values

The 22 values in the 0.6 to 7 ppm range appear to be randomly distributed through the metropolitan area with no apparent gradients. There seems to be no obvious way to draw iso-concentration lines on this figure.

The three high values are isolated. The 97 ppm result is near a wood-treating plant, where the creosote used in processing could be expected to cause the high concentration observed; the other two high values have no obvious explanation from the reported locations.

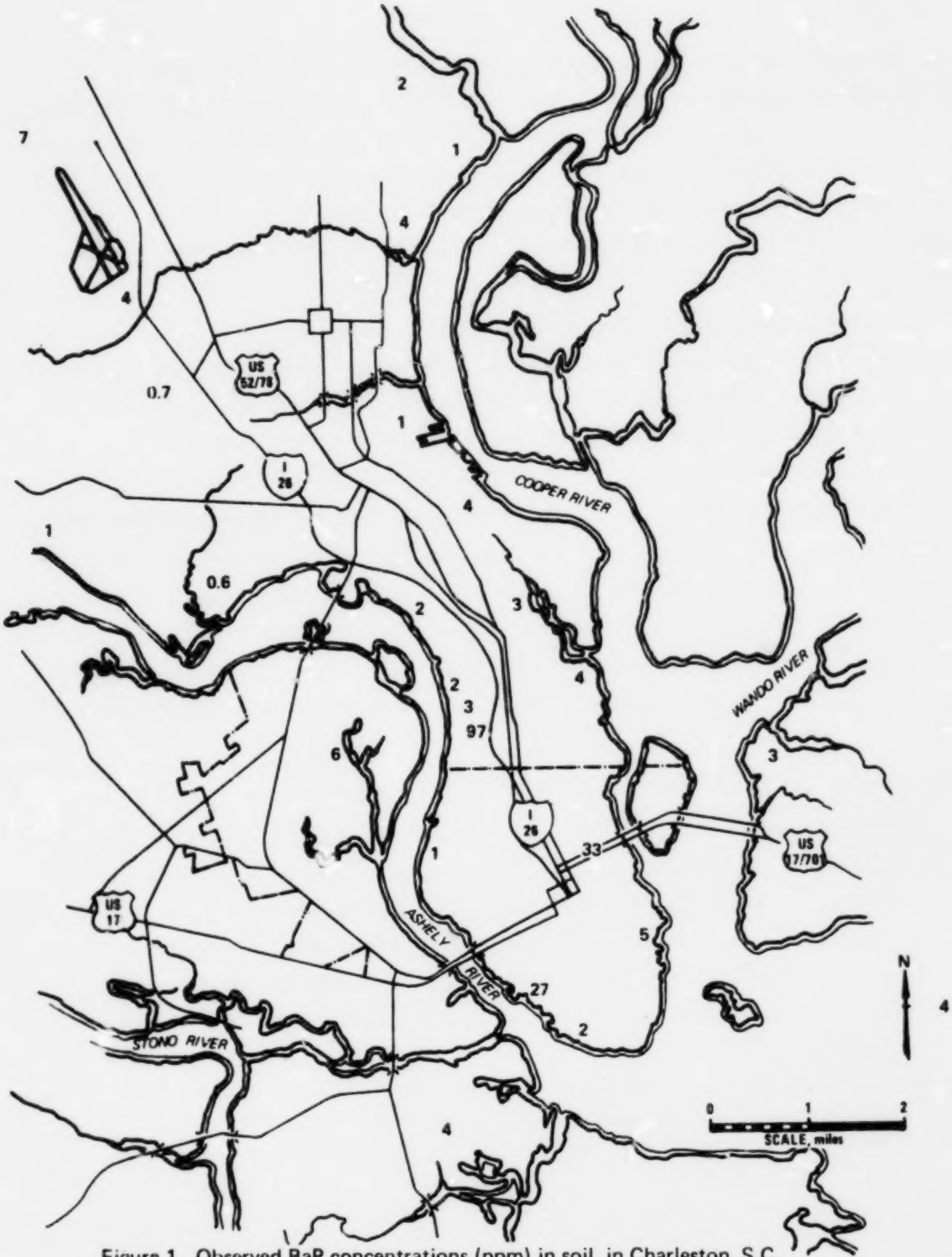

Figure 1. Observed BaP concentrations (ppm) in soil, in Charleston, S.C. (Values represent highest concentration measured at site from Table 2).

The values at the end of the runways of the airport are slightly higher than the average of the community, but not strikingly so.

It would be interesting to compare these values with those for other cities, as was done with the ambient air values, to see whether these are high, low, or average values. This is not easy to do because there are few data on soil concentrations of BaP and most of the available data are from the Soviet Union, where the mix of air pollutant emissions is probably not the same as that in the United States. (The summary indexes of Chemical Abstracts for Volumes 69-76 and 78 list a total of nine references on BaP in soils; all nine are from the Soviet Union.)

Table 5 presents a summary of reported soil concentrations of BaP. (Note that most of the Soviet sources are based on the reviews in Chemical Abstracts; except for two of them, the original sources were not consulted.) From this table it can be seen that in the Soviet Union concentrations for industrial areas are 1 to 220 ppm, for urban areas they are 0.1 to 1 ppm, and in forests they are about 0.001 ppm. The only reported value for the United States is 0.04 to 1.3 ppm in a forest area .

If these values are compared with the ones found in Charleston, the Charleston values seem to fall in the range of the other values, with no abnormally high values (except the 97 ppm near the wood-treating plant, which is not as high as that at the Soviet refinery as reported by Shabad[5]). On the other hand, the general urban values in Charleston are about an order of magnitude higher than those reported for Moscow.

ANALYSIS OF SOIL SAMPLING FOR BaP - WEST VIRGINIA

The soil samples taken in the vicinity of burning coal banks in West Virginia (summarized in Table 3) reveal values mostly in the range of 0.5 to 5 ppm of BaP. Two show values of 22 and 26 ppm. The general group of values taken near this source are not much different from those taken in Charleston. This result is surprising, in the light of published estimates[6] that burning coal refuse banks emit up to 75 percent of the total emissions of BaP in the United States. In the light of these low concentrations it can be concluded either that there is little fallout of BaP from burning coal banks in the vicinity of the source or that the estimates of the emission rates from this source are much too high.

Table 5. SUMMARY OF REPORTED SOIL CONCENTRATIONS OF BaP

Reference	Country	Location	Concentration, ppm
10	USA	Mixed forest, Conn. and Mass.	0.04 to 1.3
11	France	Forests	0.002 to 0.30
4	USSR	New building areas	0.1
		Old building areas	0.25
		Oil refinery near naphtha cracker	220
		Near an airport runway	0.01 to 0.07
		Forests	0.0001 to 0.0006
12	USSR	Various regions not described	0.0004 to 0.07
13	USSR	Moscow city	0.268 to 0.364
		Near the Moscow freeway	0.158 to 0.0668
		Various rural soils	0.001
14	USSR	Close to an industrial plant	5.5 to 8.3
		In old city territory far from industry	0.6
		In village on dead end street	0.18 to 0.52
15	USSR	200-300 meters from freeway with negligible auto traffic	0.007 to 0.089
16	USSR	Industrial areas	191

ANALYTICAL RELIABILITY

Research Triangle Institute (Appendix E) found that there was considerable difficulty making a quantitative extraction of BaP from soil samples. This organization showed that, for different extractants, the measured concentration could vary by a factor of ten. Table 2 shows that apparent duplicate samples analyzed by two different laboratories can yield results that differ by a factor of ten.

Accordingly, if soil sampling is to be undertaken in a serious way, consideration should be given to the following recommendations:

1. Analytical methods should be developed to ensure that results are meaningful.
2. Results in this report should be considered as order-of-magnitude estimates. In view of the ten-fold apparent uncertainty in the results, it seems inappropriate for the analytical laboratories to report these results to five significant figures.

HISTORICAL PROBLEM

Death rates from lung cancer probably reflect the results of long-term exposure to pollutants. Pollutant concentrations 20 years ago could have been much higher than those observed through current air- and soil-sampling programs. Therefore, mortality data for 1959-1961, which were used in this report, may not accurately reflect the effects of pollutant concentrations occurring today.

A significant program to reduce pollutant emissions took effect in the period 1968-1972. As a result of this program, the annual average concentration of suspended particulates measured at the Charleston County Health Department decreased as follows[17]:

Year	Annual average suspended particulate concentration, micrograms/m^3
1968	74.4
1969	57.9
1970	55.3
1971	44.3
1972	49.7
1973	36.7

Jacobs and Langdoc[18] linked this drop in particulate concentration with a drop in the cardiovascular death rate. (The views in that article have been reviewed critically by EPA[19].) Whether or not the views in the article are correct, they do show that pollutants are being looked at now to explain events that occurred years ago, when the pollution situation was much different.

The above particulate data indicate as much as a two-fold reduction in total suspended particulates in downtown Charleston in recent years. Even if all the measured ambient air concentrations of BaP and metals were doubled, the resulting values would still not be in the high end of the range for American cities and would not constitute strong evidence for their involvement in lung cancer. Thus, without additional historical data, the possible link between BaP and metals and lung cancer cannot be properly tested; but, given the extremely low currently measured ambient concentrations of BaP and metals, this argument must be considered speculative.

CONCLUSIONS

1. In the most recent years for which summary data are available (1959-1961), there is an anomalously high incidence of deaths from lung cancer in the Southeastern and Gulf Coast area.

2. Measured ambient air concentrations in Charleston, S.C., one of the cities with an anomalously high lung cancer death rate in 1959-1961, show that this city has a low concentration of BaP and trace metals in the ambient air. It is one of the cleaner American cities as regards these pollutants.

3. The concentration of BaP in the soil in the Charleston metropolitan area is about an order of magnitude higher than that in Moscow in the Soviet Union. There are few data from the United States with which to compare these soil concentrations. Based on comparisons with Soviet data, the Charleston values seem large but not startling.

4. Thus, the measured concentrations of BaP and trace metals found in this study do not indicate a level high enough to cause the death rate from lung cancer in Charleston to be higher than the national average.

5. The methods for analyzing BaP in soils are in need of additional refinements.

6. Results in this report should be considered as order-of-magnitude estimates.

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APPENDIX A.

STUDY OF BaP, Be, Cd, Cr, Cu, AND Ni IN AIR AT CHARLESTON, S. C., NOVEMBER 1972 THROUGH MARCH 1973

Prepared by

Geological Resources, Inc.
Raleigh, North Carolina
November 1973

INTRODUCTION

The project discussed in this report was conducted in Charleston, S. C., from November 1, 1972, until March 31, 1973, to monitor variations in the amounts of selected pollutants emitted in different sections of the city. Particulate matter was collected on glass-fiber filters by Hi-Vol samplers at three locations in Charleston--Radio Station WTMA, the Queen City Fire Station, and the Mount Pleasant Post Office (See Figure A-1). Cooperating in the collection effort were the Air Pollution Control Section of the Charleston County Health Department and the Office of Air and Water Programs, U.S. Environmental Protection Agency. Geological Resources, Inc., Raleigh, N. C., analyzed the particulate matter each week for benzo[a]pyrene, beryllium, cadmium, chromium, copper, and nickel. Results of the analyses were used to compute, for each station, the weekly average concentration of each pollutant in nanograms per cubic meter of air. During the 5-month period, which included the winter heating season, the chief meteorological factors evaluated with respect to pollution levels were temperature and wind direction variations.

ANALYSIS OF SAMPLES

Filters analyzed in the study were collected from three sampling sites during the period from November 1, 1972, to March 31, 1973, or 22 weeks. Upon collection by the Charleston County Health Department for each sampling period (approximately 1 week, with some variations), the filters were sent directly to Geological Resources, Inc. A separate composite sample for each of the three sampling stations was then made using all of the filters collected during the sampling period at that station. A total of 66 composite samples were analyzed for benzo[a]pyrene (BaP), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), and nickel (Ni) for a total of 396 separate analyses.

The composite samples for analysis were prepared in accordance with procedures outlined in Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption.[1] Metals were determined, using standard procedures, with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Benzo[a]pyrene was determined through techniques of thin-layer chromatography and spectrofluorometry, again with standard procedures of preparation.

Results of analyses for BaP and metals are given in the addendum.

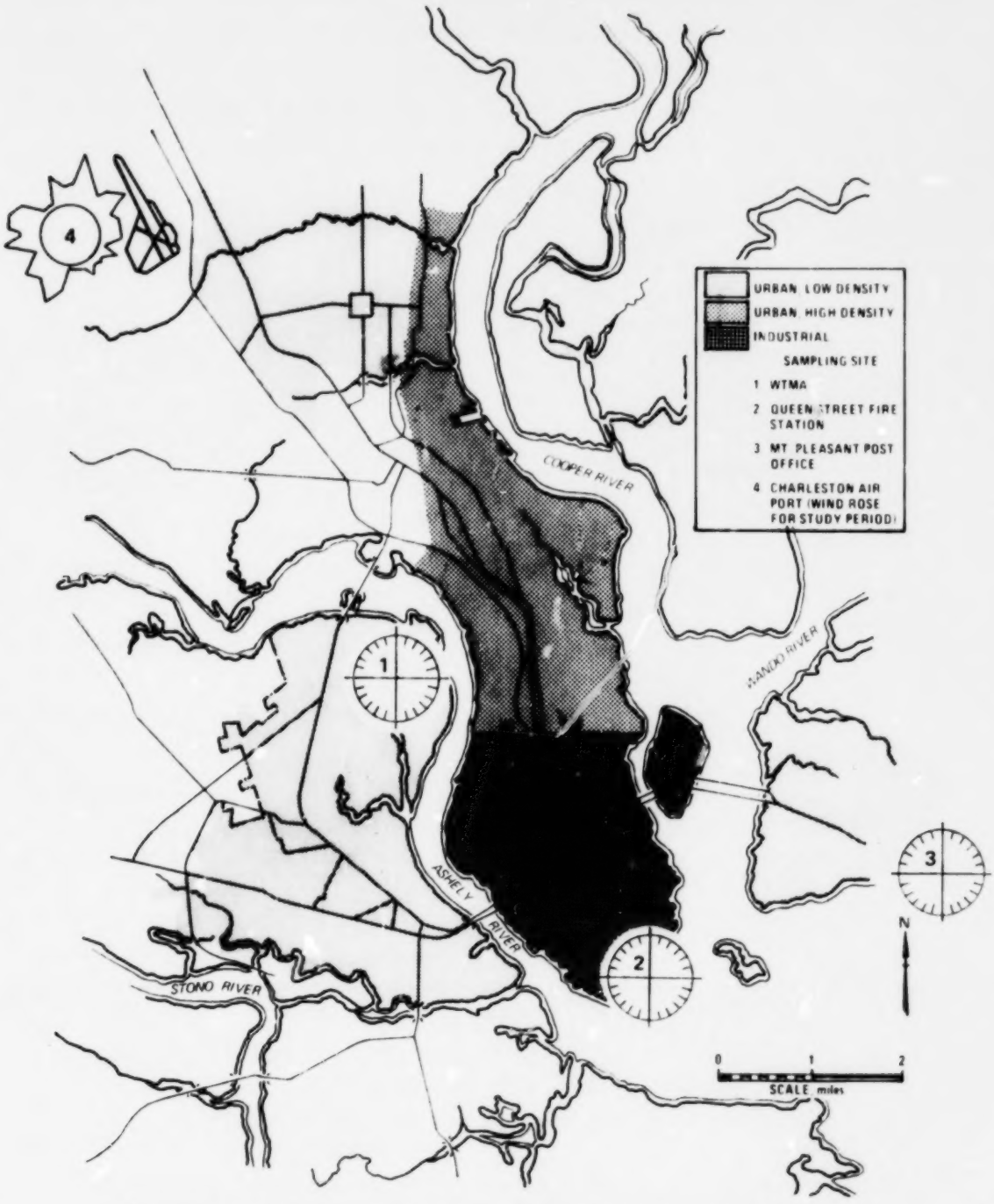

Figure A-1. Outline map of Charleston, S.C., showing locations of air sampling sites.

DISCUSSION OF DATA

Air Pollution Levels at Three Sampling Sites in Charleston

Table A-1 shows average amounts of benzo[a]pyrene and five metals in air during the study period at the three sampling sites. Comparison of analyses made during the study with published data on air pollution at other urban areas along the mid-Atlantic coast during the same time of year (Table A-2) indicates that the amounts of Be, Cd, and Cr in the air at Charleston are somewhat less than measured quantities at the other cities. BaP, Cu, and Ni pollution in the air at Charleston is on about the same level as in other similar urban areas.

Table A-1. AVERAGE AIRBORNE CONCENTRATIONS OF BaP AND FIVE METALS AT CHARLESTON, NOVEMBER 1, 1972 to MARCH 31, 1973 (ng/m^3)

Pollutant	WTMA	Queen Street Fire Station	Mount Pleasant Post Office
BaP	0.5711	0.7441	0.7448
Be	0.0373	0.0287	0.0363
Cd	0.2751	0.3024	0.2531
Cr	0.7293	0.5870	0.3589
Cu	62.9	59.0	47.2
Ni	0.8332	0.8306	0.6359

Table A-2. RANGE OF VALUES FOR SELECTED AIR POLLUTANTS DURING WINTER MONTHS AT CHARLESTON AND SELECTED MID-ATLANTIC CITIES[2] (ng/m^3)

Pollutant	Range of concentrations			
BaP	0.003-2.22	Charleston	1.4-3.63	Norfolk, Va.
Be	0.000-0.161	Charleston	0.00-2.0	Norfolk, Va.
Cd	0.114-0.924	Charleston	0.00-20.0	Baltimore, Md.
Cr	0.000-2.15	Charleston	130-180 (1.0-8.0	Baltimore, Md. Greenville, S. C.)
Cu	8.9-253.4	Charleston	34.0-81.0	Norfolk, Va.
Ni	Trace-2.48	Charleston	1-12	Portsmouth, Va.

In general, metal contamination in the air was highest at Radio Station WTMA and was lowest at the Mount Pleasant Post Office. On the other hand, BaP was lowest in air at the radio station and highest at the post office. Air at the Queen Street Fire Station had a pollution level generally intermediate in relation to the other two sites. Table A-3 summarizes these observations.

Table A-3. RELATIVE AIR POLLUTION LEVELS AT THREE SAMPLING STATIONS IN CHARLESTON, NOVEMBER 1, 1972, TO MARCH 31, 1973

Pollutant	Highest	Intermediate	Lowest
BaP	Post office	Fire station	Radio station
Be	Radio station	Post office	Fire station
Cd	Fire station	Radio station	Post office
Cr	Radio station	Fire station	Post office
Cu	Radio station	Fire station	Post office
Ni	Radio station	Fire station	Post office

As shown in Figure A-1, Radio Station WTMA, the site with the highest levels of most metal air pollutants, is closer to the industrial section of Charleston; the Mount Pleasant Post Office, with the lowest metal air pollutant values, is farthest from the industrial section. Jacobs and Langdoc[3] point out that practically all major sources of industrial air pollution are located in this section of Charleston. Major industries there include fertilizer plants, a kraft papermill, a ferroalloy plant, a chemical complex, and military bases. Based on the principle that pollutants in air tend to become diluted as they move with the wind out from their sources,[4] it appears that activities in the industrial section of Charleston result in release of some metal pollutants to the air.

The cause for the lower levels of BaP in the air at the radio station, compared with the other two sampling sites, may be related to the station being located in an area with lower traffic activity and fewer houses, both of which contribute BaP to the atmosphere through fuel combustion.[5]

Variation of Air Pollution Levels During Study

Variations in the level of pollutants in the air at each of the three sampling stations are shown in Figures A-2 through A-7. BaP, Be, Cd, and Ni levels in the air tended to increase at the beginning of the study period and to decrease toward the end of the period. Average temperatures at Charleston showed a decline at the beginning of the period and an increase at the end. Comparison of temperature variations during the period of study (Figure A-8) with levels of BaP, Be, Cd, and

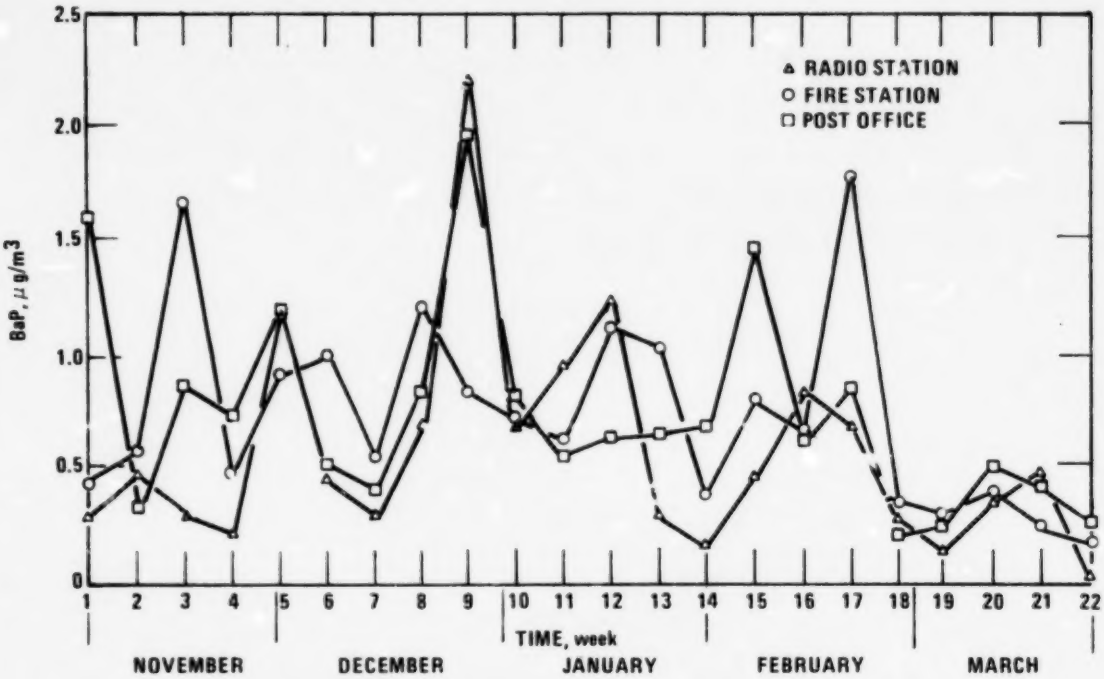

Figure A-2. Weekly average BaP content of air at three sampling sites in Charleston, S.C., November 1, 1972, to March 31, 1973.

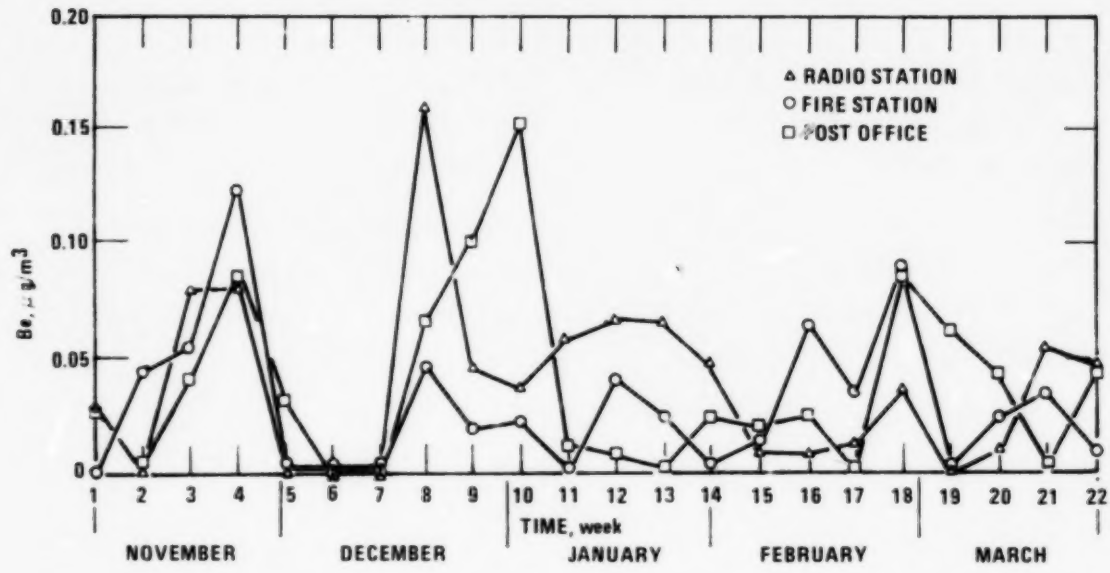

Figure A-3. Weekly average Be content of air at three sampling sites in Charleston, S.C., November 1, 1972, to March 31, 1973.

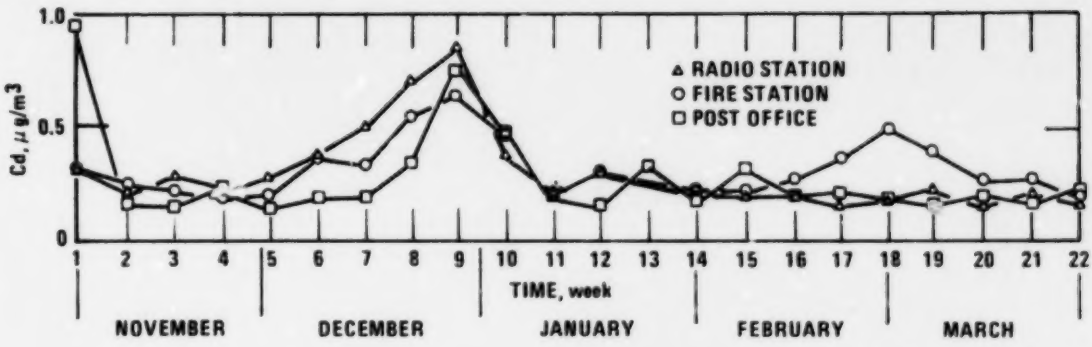

Figure A-4. Weekly average Cd content of air at three sampling sites in Charleston, S.C., November 1, 1972 to March 31, 1973.

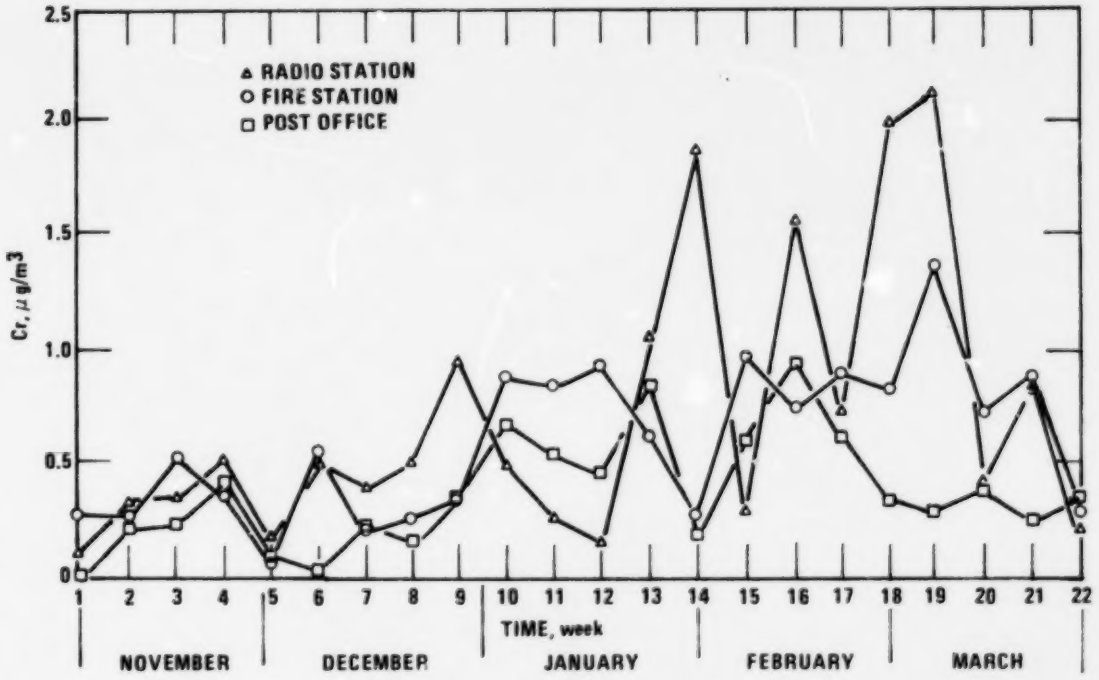

Figure A-5. Weekly average Cr content of air at three sampling sites in Charleston, S.C., November 1, 1972 to March 31, 1973.

Ni suggests a reasonably good (inverse) correlation of colder weather with higher levels of these pollutants. BaP variations correlate best with temperature fluctuations. Because combustion of fuels is a potential source of BaP[5] and certain metals,[6] the probability is that increased combustion of fuels during cold weather leads to higher concentrations of these pollutants in the air.

Although the burning of both solid and liquid fuels releases BaP and various metals, this is not likely to be the only source of these pollutants at Charleston. A

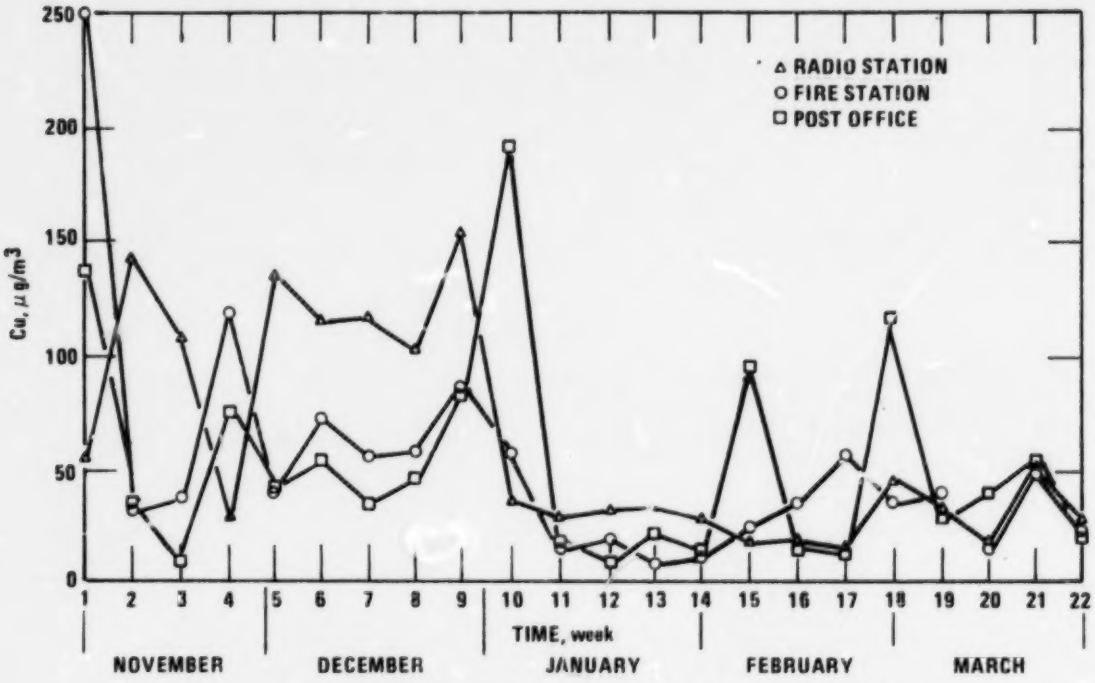

Figure A-6. Weekly average Cu content of air at three sampling sites in Charleston, S.C., November 1, 1972 to March 31, 1973.

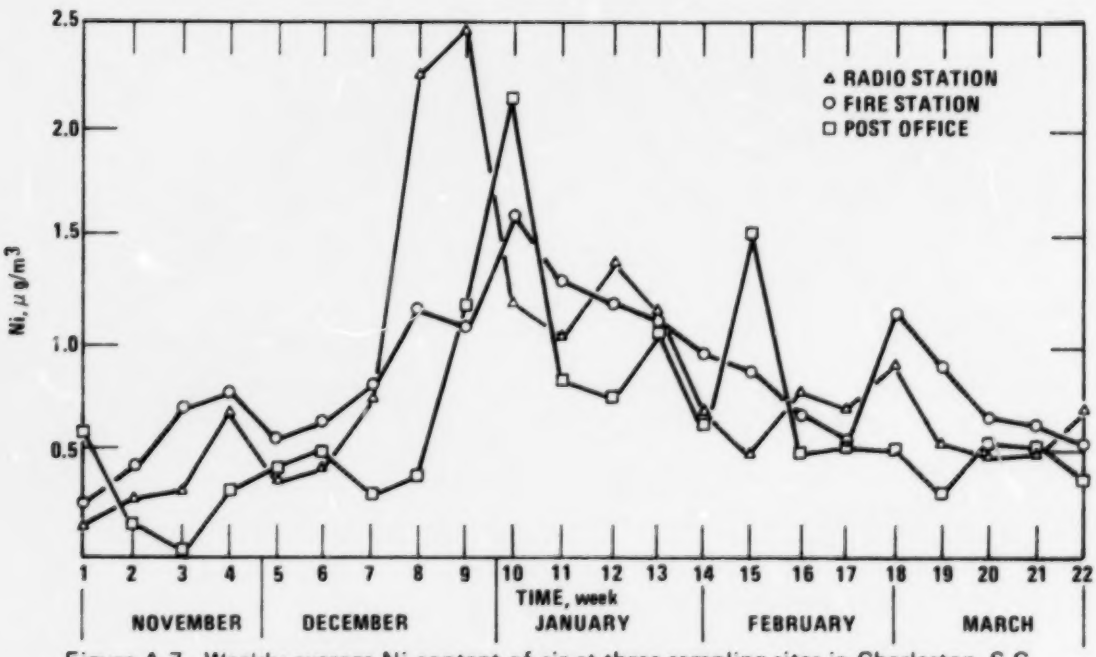

Figure A-7. Weekly average Ni content of air at three sampling sites in Charleston, S.C., November 1, 1972 to March 31, 1973.

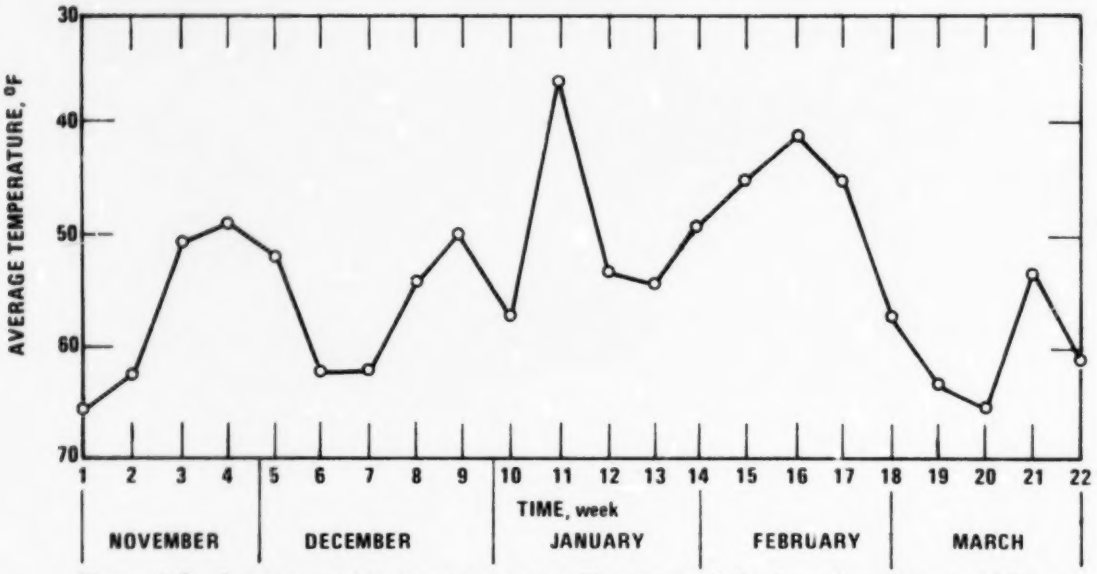

Figure A-8. Average weekly temperatures at Charleston, S.C., from November 1, 1972 to March 31, 1973.[7]

comparison of BaP values and metal values in air at the Mount Pleasant Post Office and Radio Station WTMA (Table A-1) indicates that the ratio of metals to BaP is not constant. Thus, separate sources must account for some of the individual pollutants.

The levels of Cr and Cu in the air at Charleston during the study period exhibited patterns different from the other air pollutants studied. Cr continued to increase in the air until late February and early March before beginning a decline. Cu levels showed a general decline throughout the period, with a low in January. Because Cu and Cr levels in the air were higher at the radio station than at the other two sites, and because the radio station is closer to the industrial section of Charleston, it is possible that the variations in levels of these substances reflect, to some degree, variations in industrial processes and/or activities.

Air Pollution Level Variations and Wind

The purpose of combining wind data with air pollution in the study was to determine whether certain wind directions tended to increase air pollution levels at the three Hi-Vol air sampling sites. This aspect of the investigation has some limitations. Wind speed effects are not integrated into the study even though high speed winds will be less contaminated when passing over a pollution source than will low speed winds moving in the same direction over the same source.[8] Wind direction data as recorded by the National Weather Service Office at the Charleston Municipal

Airport do not agree with the directions observed at each of the sampling sites. Table A-4 illustrates these differences during the first week of the study period.

Table A-4. WIND DIRECTION OBSERVATIONS RECORDED AT HI-VOL AIR SAMPLING SITES AND AT CHARLESTON MUNICIPAL AIRPORT, 1972

Date	National Weather Service observations[a]	Observations at air sampling sites		
	Airport	Radio station	Fire station	Post office
Nov. 1	100	180	135	180
Nov. 2	180	135	180	80
Nov. 3	230	225	225	225
Nov. 4	260	225	225	
Nov. 5	50	45	45	
Nov. 6	80	135	225	135

[a]Local climatological data for Charleston.

Differences in wind directions recorded at the three sites probably resulted from differences in time of observation: Hi-Vol air sampling sites were observed only once each day, at the time air filters were changed, and this time varied from site to site. Furthermore, winds observed at Hi-Vol air sampling sites located within a few feet of the ground probably reflect local turbulence.[9] On the other hand, wind directions recorded at the airport are "resultant winds" based on several observations each day. Because of the arrangement of weather instruments, these values are more likely to reflect true wind directions over the entire city. For these reasons, it was decided to use airport wind-direction data rather than sampling site wind data.

Examination of the curves shown in Figure A-2 through A-7 reveals that air pollution levels for a given substance at the three Hi-Vol air sampling sites vary rather similarly during the entire period of study. Detailed examination also shows, however, that during a given week the pollution level may be relatively high at one sampling site and relatively low at the other two. For example, note in Figure A-2 that during the first and fifteenth weeks of the study period BaP was relatively high at the post office and relatively low at the other two sites. Plotting wind directions during days in which air pollutant levels are relatively high less the days in which pollution levels are relatively low at each of the three Hi-Vol air sampling sites has resulted in the "pollution wind roses" shown in Figures A-9 through A-14.

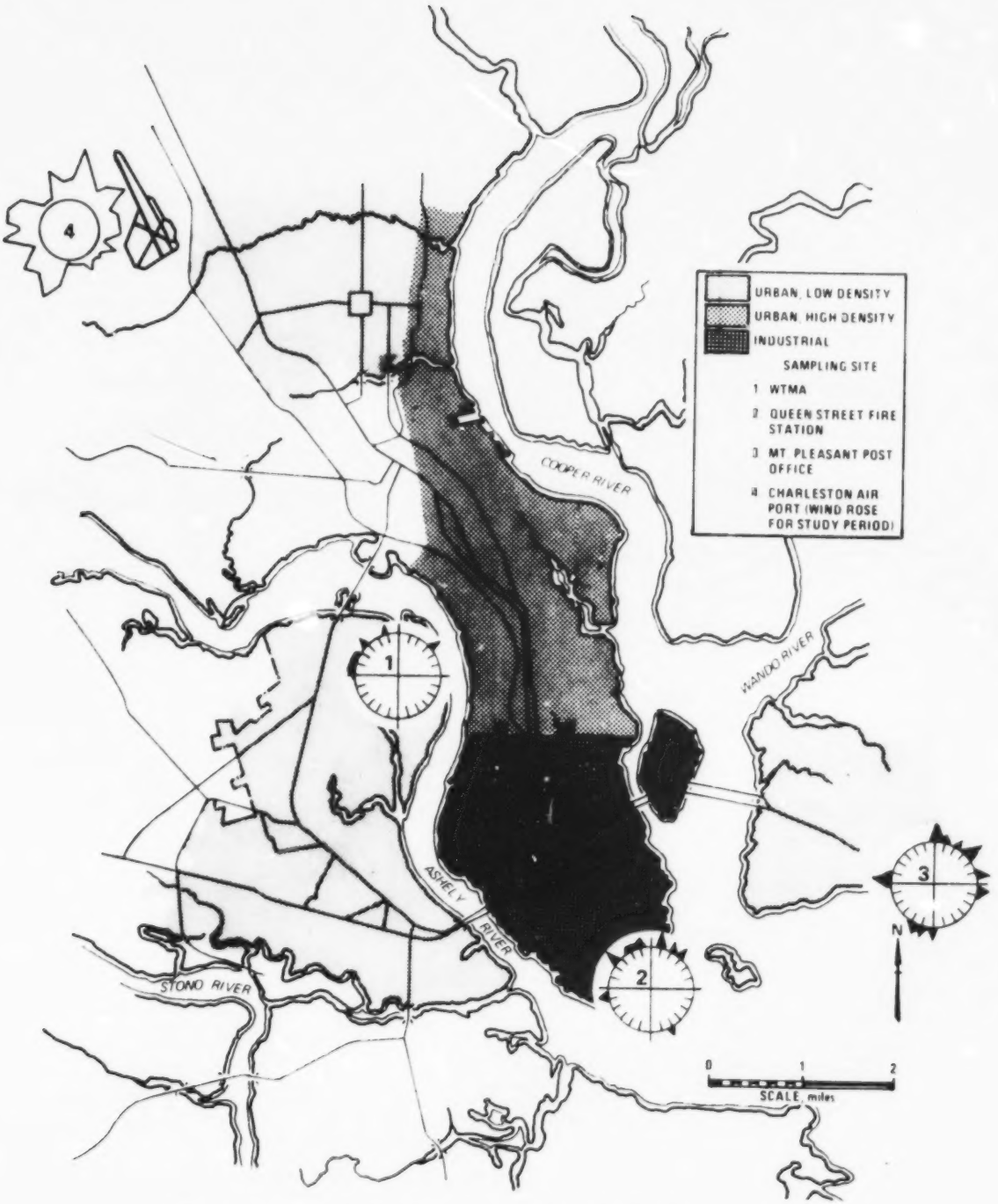

Figure A-9. Wind roses for days during which BaP content of air was relatively high at sampling stations.

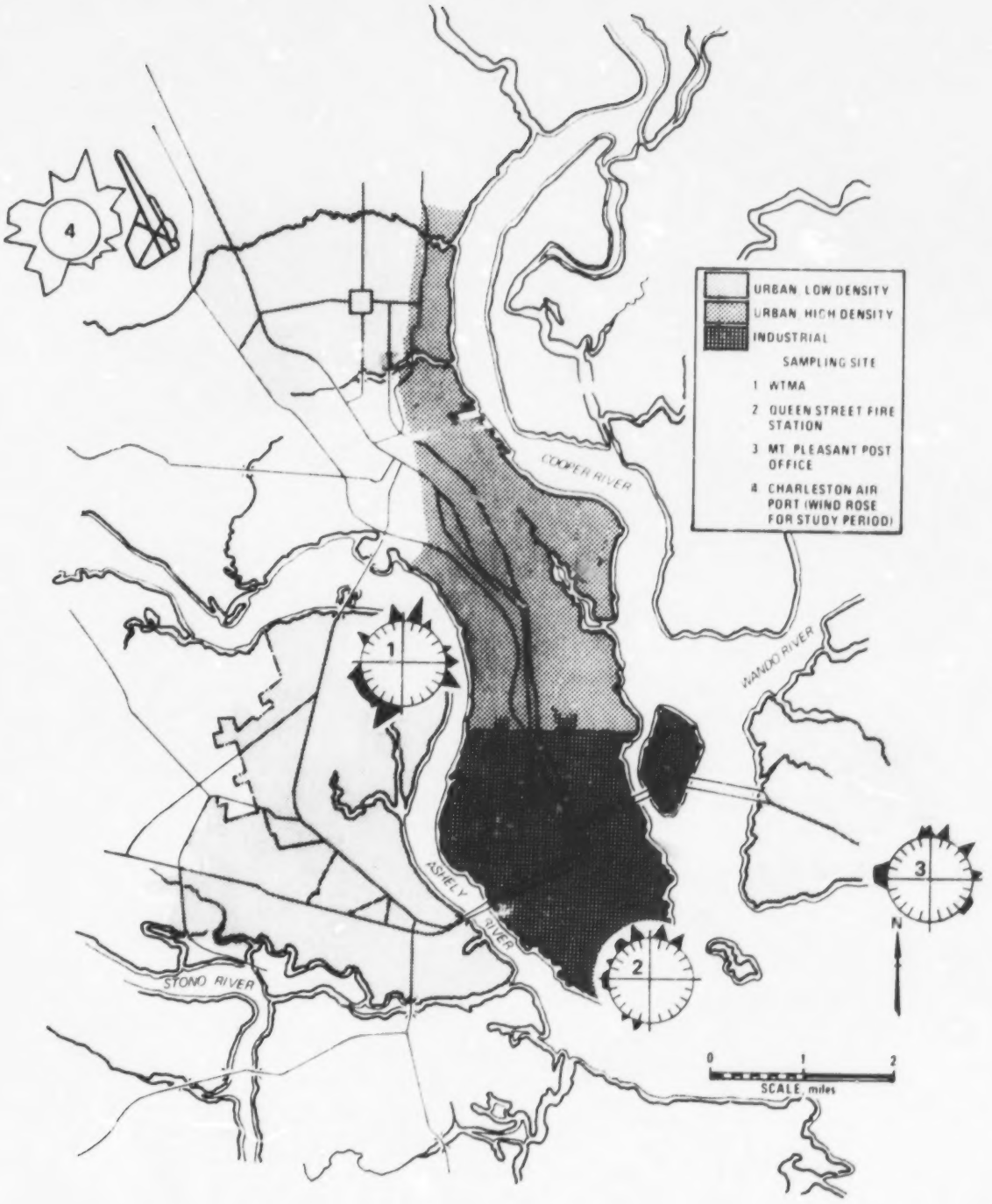

Figure A-10. Wind roses for days during which Be content of air was relatively high at sampling stations.

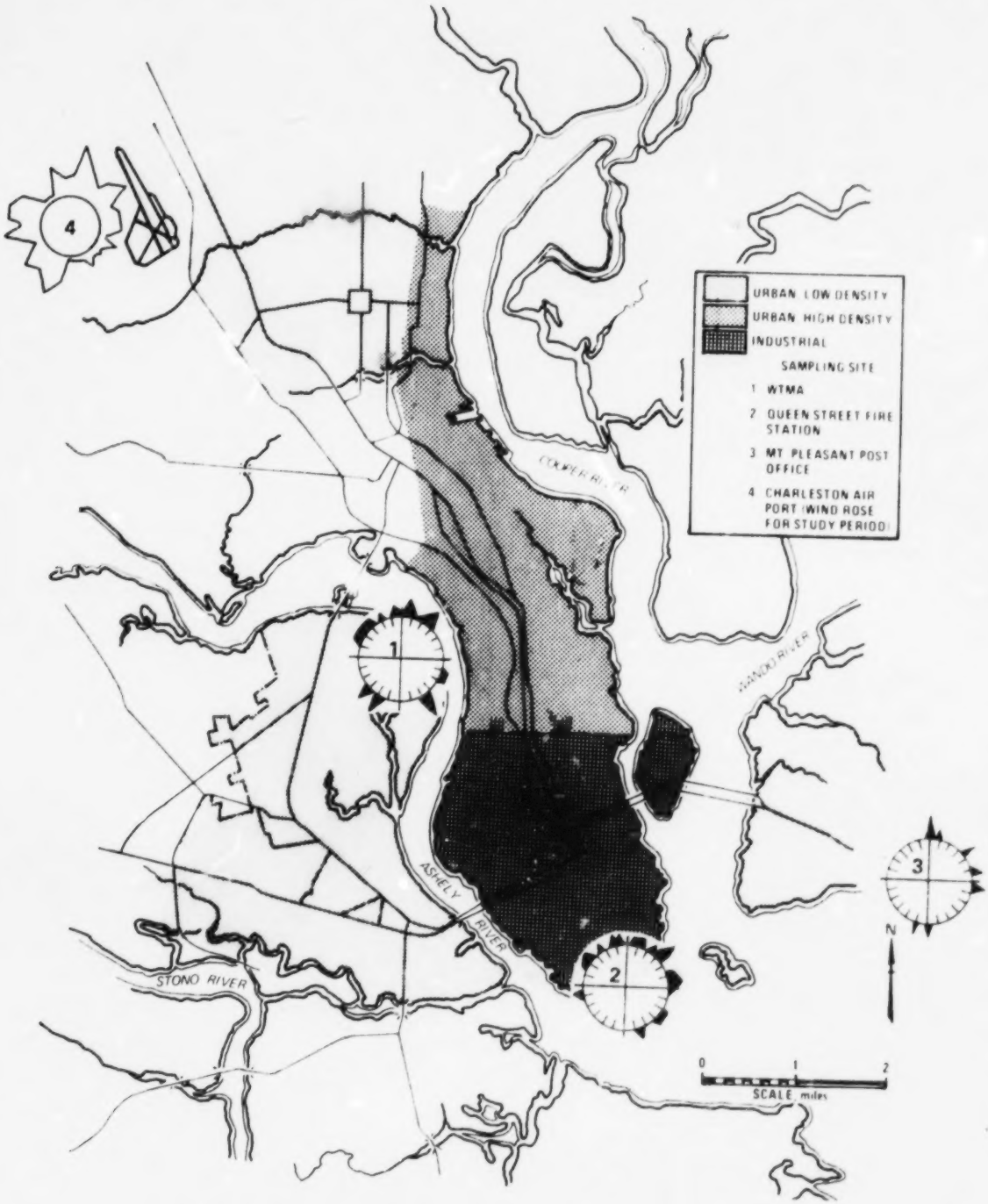

Figure A-11. Wind roses for days during which Cd content of air was relatively high at sampling stations.

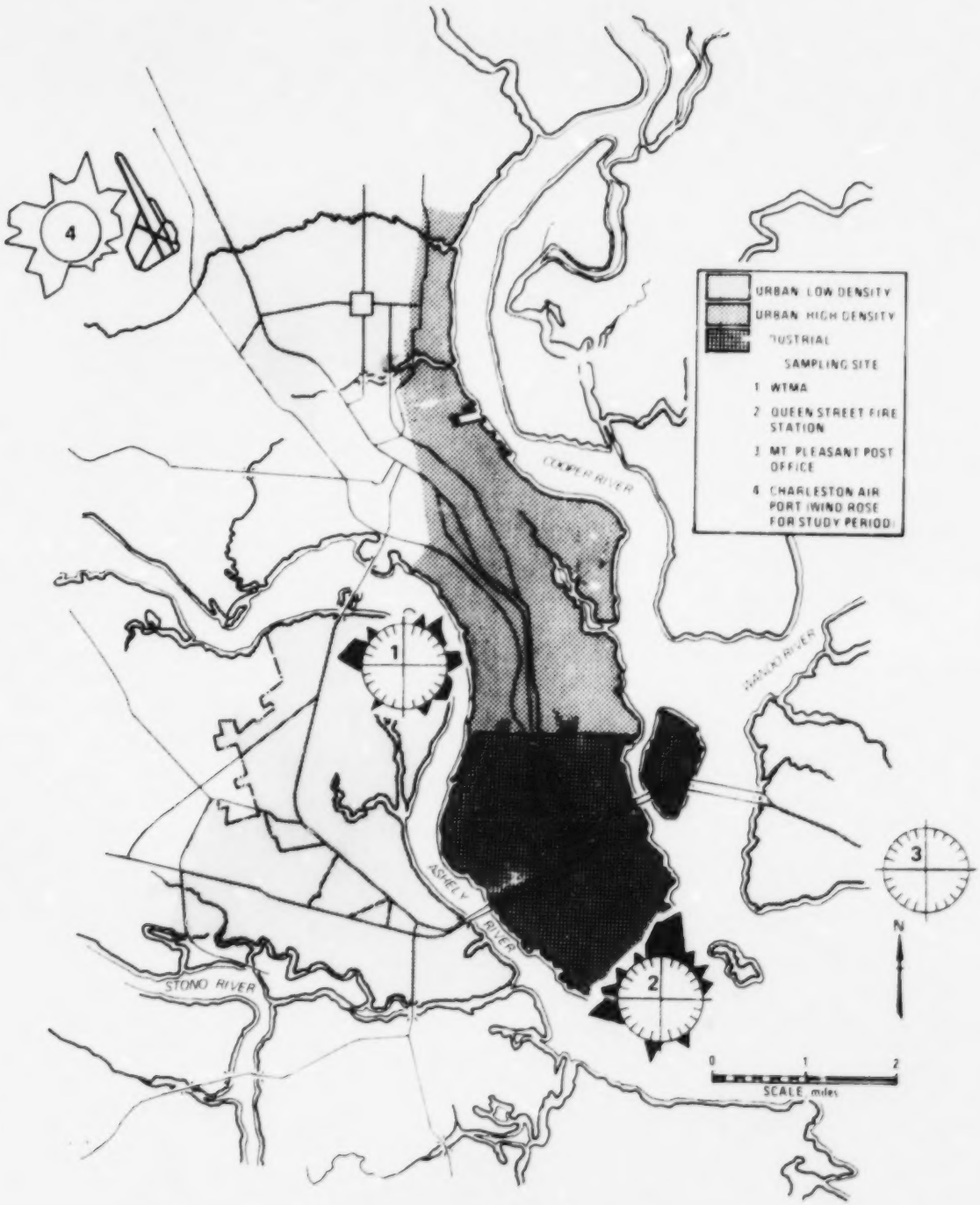

Figure A-12. Wind roses for days during which Cr content of air was relatively high at sampling stations.

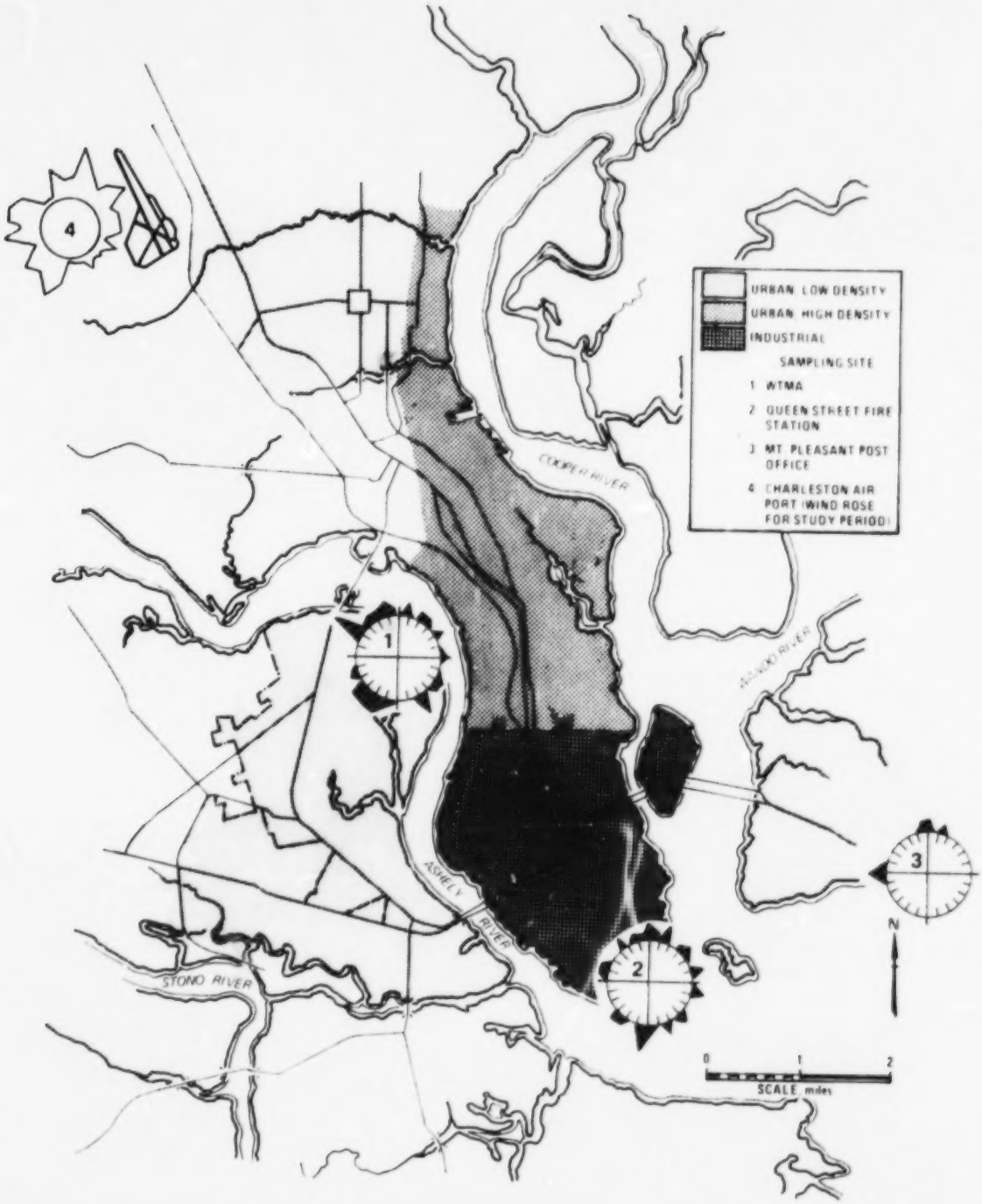

Figure A-13. Wind roses for days during which Cu content of air was relatively high at sampling stations.

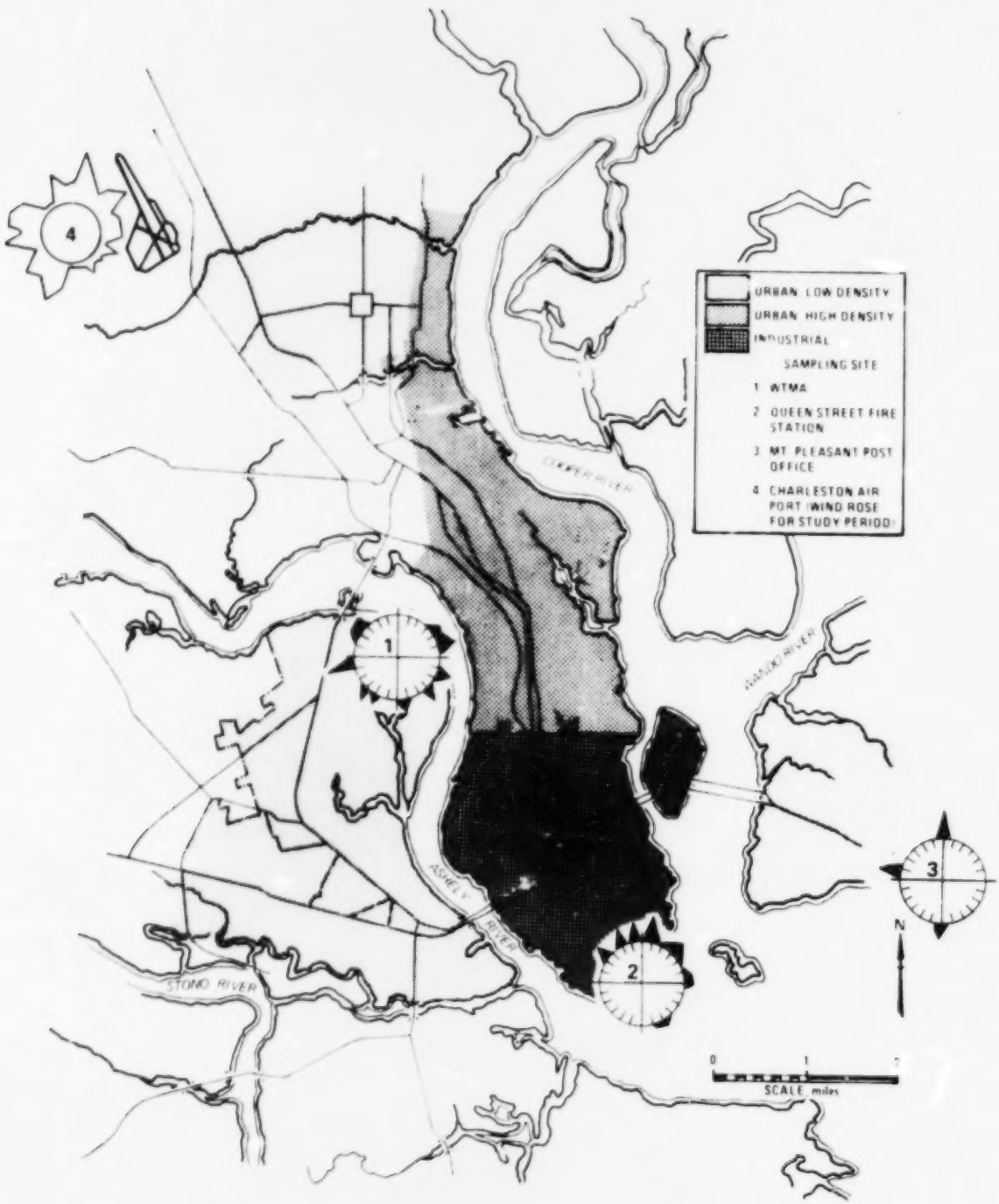

Figure A 14. Wind roses for days during which Ni content of air was relatively high at sampling stations.

Examination of the pollution wind roses suggests that the tentative conclusions listed in Table A-5 may be made concerning general source directions for pollutants at each of the three Hi-Vol air sampling sites.

Table A-5. POSSIBLE SOURCE DIRECTIONS FOR AIR POLLUTANTS AT THREE HI-VOL AIR SAMPLING SITES IN CHARLESTON, S.C., NOVEMBER 1, 1972, to MARCH 31, 1973

Sampling site	Pollutant	Wind direction
Radio station	BaP	W, NW
	Cr, Ni	W, E
	Be, Cd, Cu	Random
Fire station	BaP	N
	Be, Cr	N, W
	Ni	N, E
	Cd, Cu	Random
Post office	Cu	N, W
	Ni	N, W, S
	Cd	N, E, S
	BaP	Random
	Cr	All directions low

Although this analysis of wind direction effects on levels of air pollution at the different air sampling sites has limitations, in a general sense many of the pollution wind roses (for example Cr and Ni) point toward Charleston's industrial section. The positions of major traffic arteries and high-density housing areas, which are also sources of air pollution, obviously increase the number of directions from which winds could bring pollution to a given site.

SUMMARY

1. The amounts of Be, Cd, and Cr in the air at Charleston are somewhat less than those quantities in urban areas along the mid-Atlantic coast. BaP, Cu, and Ni pollution is on about the same level as in other similar urban areas.

2. Be, Cr, Cu, and Ni were found to be present in air in greater quantities closer to the industrial section of the Charleston Peninsula, north of the city.

3. Higher amounts of BaP in air appear to be correlative with higher densities of nearby traffic and housing.

4. BaP, Be, Cd, and Ni tend to increase in the air at Charleston during periods of colder weather, suggesting that combustion of fuels contributes significantly to the presence of the metals in the air. However, because the ratio of these metals

to BaP is not constant from site to site, there must be separate sources for some of the individual pollutants.

5. The levels of Cr and Cu in air during the study period exhibit patterns different from the other air pollutants studied. Because their levels are highest in air near Charleston's industrial section, it is possible that the variations in levels of these substances reflect, to some degree, variations in industrial processes and/or activities.

6. Analysis of wind direction data and pollution levels at the sampling sites during the study period suggests that the industrial section of Charleston contributes significantly to air pollution in that city but that other sources of air pollution, not identified, also exist.

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ADDENDUM

Weekly average benzo[a]pyrene, beryllium, cadmium, chromium, copper, and nickel concentrations for Charleston are given in Table A-6.

Table A-6. WEEKLY AVERAGE BaP AND METAL CONTENTS OF AIR AT THREE SAMPLING SITES IN CHARLESTON, S.C., NOVEMBER 1, 1972, TO MARCH 31, 1973
(ng/m^3)

Date and Site	BaP	Be	Cd	Cr	Cu	Ni
11/1/72-11/8/72						
Radio station	0.2882	0.0275	0.2444	0.0916	55.0	0.1466
Fire station	0.4450	0	0.2419	0.2547	253.4	0.2610
Post office	1.6162	0	0.9245	0	139.8	0.5926
11/8/72-11/15/72						
Radio station	0.4692	0.0022	0.1778	0.3174	145.7	0.2753
Fire station	0.5852	0.0452	0.2157	0.2575	33.4	0.3410
Post Office	0.3462	0.0018	0.1237	0.2199	30.7	0.1328
11/15/72-11/22/72						
Radio station	0.2865	0.0820	0.2521	0.3401	110.2	0.3049
Fire station	1.6787	0.0574	0.1850	0.5105	8.9	0.7019
Post office	0.8822	0.0400	0.1242	0.2346	38.0	Trace
11/22/72-11/29/72						
Radio station	0.2087	0.0816	0.1865	0.5130	28.0	0.6938
Fire station	0.4900	0.1247	0.1662	0.3637	119.5	0.7586
Post office	0.7457	0.0863	0.2158	0.4058	75.1	0.3194
11/29/72-12/5/72						
Radio station	1.1882	0	0.2433	0.1520	138.4	0.3650
Fire station	0.9227	0	0.1594	0.0797	40.4	0.5524
Post office	1.1977	0.0312	0.1136	0.0965	41.5	0.3863
12/5/72-12/10/72						
Radio station	0.4496	0	0.3636	0.4990	117.6	0.4063
Fire station	1.0842	0	0.3752	0.5369	73.1	0.6274
Post office	0.5055	0	0.1688	Trace	55.9	0.4741
12/11/72-12/16/72						
Radio station	0.3014	0	0.4565	0.3701	120.9	0.7279
Fire station	0.5598	0	0.3016	0.2077	56.3	0.7640
Post office	0.4138	0	0.1737	0.2004	36.1	0.2605
12/18/72-12/22/72						
Radio station	0.6973	0.1609	0.6438	0.4829	103.0	2.2535
Fire station	1.2265	0.0464	0.5339	0.2205	58.0	1.1490
Post office	0.8368	0.0665	0.3162	0.1414	47.4	0.5575
12/27/72-12/30/72						
Radio Station	2.2217	0.0467	0.8232	0.9354	155.3	2.4883
Fire station	0.8390	0.0162	0.6328	0.3083	84.4	1.0872
Post office	1.9767	0.1013	0.7167	0.3321	89.2	1.1713
1/1/73-1/6/73						
Radio station	0.6850	0.0355	0.3831	0.4868	38.1	1.1963
Fire station	0.7147	0.0211	0.4756	0.8667	59.7	1.6172
Post office	0.8390	0.1529	0.4905	0.6626	195.0	2.1662
1/7/73-1/14/73						
Radio station	0.9448	0.0605	0.1874	0.2418	28.4	1.0279
Fire station	0.6413	0	0.1859	0.8337	14.0	1.2699
Post office	0.5619	0.0114	0.1901	0.5388	14.9	0.8241

Table A-6 (continued). WEEKLY AVERAGE BaP AND METAL CONTENTS OF AIR AT THREE SAMPLING SITES IN CHARLESTON, S.C., NOVEMBER 1, 1972, TO MARCH 31, 1973 (ng/m^3)

Date and Site	BaP	Be	Cd	Cr	Cu	Ni
1/14/73-1/19/73						
Radio station	1.2409	0.0686	0.2791	0.1234	33.3	1.3711
Fire station	1.1366	0.0408	0.2898	0.9226	19.6	1.2084
Post office	0.6491	0.0061	0.1478	0.4368	11.4	0.7392
1/22/73-1/27/73						
Radio station	0.2835	0.0661	0.2495	1.0641	35.2	1.1375
Fire station	1.0435	0.0241	0.2526	0.6015	10.0	1.0908
Post office	0.6684	0	0.3091	0.8329	24.9	1.0734
1/28/73-2/4/73						
Radio station	0.1568	0.0473	0.2284	1.8923	30.2	0.6899
Fire station	0.3759	0	0.2282	0.2381	11.9	0.9593
Post office	0.6818	0.0216	0.1507	0.1762	12.3	0.6369
2/4/73-2/11/73						
Radio station	0.4581	0.0108	0.1569	0.2543	24.4	0.4871
Fire station	0.8163	0.0109	0.1966	0.9614	06.7	0.8740
Post office	1.4852	0.0186	0.2996	0.5476	22.2	1.5188
2/11/73-2/17/73						
Radio station	0.8396	0.0069	0.1994	1.5573	20.9	0.7596
Fire station	0.6832	0.0644	0.2525	0.7361	35.3	0.6809
Post office	0.6346	0.0238	0.2008	0.9413	15.7	0.4706
2/20/73-2/24/73						
Radio station	0.6925	0.0057	0.1382	0.7225	16.0	0.6910
Fire station	1.8191	0.0332	0.3390	0.8753	61.9	0.5520
Post office	0.8601	0	0.1842	0.6087	16.0	0.6007
2/26/73-3/3/73						
Radio station	0.2740	0.0357	0.1667	2.0752	47.0	0.9052
Fire station	0.3484	0.0886	0.4818	0.8103	120.5	1.1497
Post office	0.1995	0.0848	0.1574	0.3088	38.2	0.5147
3/4/73-3/10/73						
Radio station	0.1329	0	0.2069	2.1474	39.3	0.5579
Fire station	0.2711	0	0.3764	1.3573	40.3	0.9119
Post office	0.2658	0.0624	0.1299	0.2646	34.3	0.2963
3/12/73-3/17/73						
Radio station	0.3553	0.0064	0.1308	0.3701	17.2	0.4723
Fire station	0.3914	0.0230	0.2296	0.7043	16.8	0.6890
Post office	0.5037	0.0434	0.1581	0.4092	41.2	0.5084
3/19/73-3/24/73						
Radio station	0.4509	0.0529	0.1488	0.8399	53.2	0.4827
Fire station	0.2462	0.0337	0.2487	0.8345	55.8	0.6018
Post office	0.4263	0	0.1313	0.2188	58.2	0.5002
3/26/73-3/31/73						
Radio station	0.0028	0.0431	0.1267	0.1534	28.2	0.6655
Fire station	0.1693	0.0060	0.1590	0.2451	23.5	0.5167
Post office	0.2367	0.0429	0.1925	0.3219	23.5	0.3472

APPENDIX B.
ANALYSIS OF BENZO[a]PYRENE IN SOIL SAMPLES

Prepared by

Research Triangle Institute
Research Triangle Park, North Carolina

January 1973

FOREWORD

This report, which is presented as Appendix B, was prepared by members of the Engineering Division of the Research Triangle Institute, Research Triangle Park, North Carolina, for the National Source Inventory Section, Applied Technology Division, Environmental Protection Agency.

The work was performed by the Instrumentation, Measurements, and Device Research Department under the general supervision of Mr. J.B. Tommerdahl, Manager. Mr. C.E. Decker was Project Leader. Mr. D.E. Wagoner provided the technical support required to complete this task and is the author of this report. Mr. R.T. Pickett assisted in the analysis of benzo[a]pyrene in soil samples.

Analysis of soil samples was conducted under two EPA purchase orders (Number 2PO-68-6424 and Number 3-02-00692), which were completed separately but which were combined for presentation in this document. The same sample handling and analytical procedures were used in both projects.

INTRODUCTION

The objective of this work was to analyze soil samples for their benzo[a]pyrene (BaP) content using EPA's current method for analysis of BaP in extracts of airborne particulates. Nine samples were initially submitted by Mr. Carl V. Spangler, Project Monitor, under Purchase Order No. 2PO-68-02-6424; subsequently, several samples were extracted and analyzed for a second determination. Additional soil samples were analyzed under Purchase Order No. 3-02-00692. Modifications were applied to the analytical procedure as required to improve separation of BaP from other organic materials by thin-layer chromatography. Alternative procedures other than Soxhlet extraction with benzene for removal of BaP from the soil samples were investigated at the request of the project monitor.

ANALYTICAL PROCEDURE

The procedure employed for the analysis of BaP in soils was adapted from EPA's current procedure for analysis of BaP in extracts of airborne particulates. This procedure involves Soxhlet extraction of BaP with benzene, thin-layer chromatographic separation of BaP from other organics, and quantitation of BaP by measurement of fluorescence emission at 540 nanometers (nm).

Initial Procedure for Analysis of Benzo[a]pyrene
in Soil Samples as Supplied by EPA

1. Soil samples will be thoroughly mixed, freed from foreign material, and dried at room temperature and normal pressure. One-hundred-fifty grams (g) of the soil will be crushed thoroughly and divided into two 50-g portions and five 10-g portions. Samples will be placed in filter cups that have been previously extracted with diethyl ether under reflux.

2. An appropriate sample (10- or 50-g sample) will be refluxed for a period of 8 hours with benzene in a Soxhlet apparatus.

3. The resulting benzene solution will be reduced in volume on a steam bath located in a hood.

4. The sample will be filtered through a sintered glass funnel into a previously weighed test tube, dried under vacuum at 60°C, and weighed.

5. The benzene soluble fraction will be dissolved in methylene chloride (1.0 milliliter/25 milligrams of residue). The test tube will be capped and sample allowed to dissolve.

6. Eighty microliters of the methylene chloride solution will be spotted on an aluminum oxide (Al_2O_3) thin layer plate that has been activated at 110°C and stored in a dessicator over phosphorous pentoxide. In addition to the sample, a standard of benzo[a]pyrene will be run simultaneously.

7. The plate will be placed in a developing tank with the appropriate solvent to effect a complete separation of BaP from the other constituents.

8. The plate, while still moist, will be removed and placed in an ultraviolet viewing chamber. The sample spot corresponding to BaP plus the standard will be scribed.

9. The spots will be scraped onto glassine paper and transferred to a dry, screwcap vial tube containing 8 ml of pentane/acetone (95/5). The vials will be shaken (> 10 minutes) and allowed to settle. The supernatent liquid will be transferred through a coarse porosity sintered glass funnel into a dry, screwcap test tube. The adsorbent will be washed with additional portions of pentane/acetone and all portions combined. Test tubes will be evaporated (in water bath at 35 to 40°C) in a vacuum oven at approximately 50 torr, until the solvent is evaporated. The sample will be dried in a vacuum oven without water bath for at least 10 additional minutes.

10. The fluorimeter will be blanked with concentrated sulfuric acid. Five ml of concentrated sulfuric acid will be added to each sample tube and 10.0 ml to the standard test tube. The test tubes will be stoppered and shaken to allow bubbles to escape (approximately 5 minutes) and transferred to a cuvette. The fluorescence is read in a filter fluorimeter. Fluorimeter setting will be as follows: excitation wavelength = 470 nm; emission wavelength = 540 nm.

Identification will be by comparison of relative R_f values of pure BaP versus R_f values of the experimental samples. The concentration of BaP in soil will be determined by comparing the fluorescence of the sample solution with the fluorescence of a sulfuric acid solution of a standard amount of BaP that has been carried through the thin-layer chromatograph and elution steps.

Adapted Procedure

The following sample handling and analytical procedures were initiated after discussion with the project monitor. (Preliminary precautions included storing samples in boxes protected from light after delivery to RTI by EPA and storing samples, when not under investigation, in a refrigerator - this includes interim steps in the analysis.)

1. Soil samples are dried at room temperature in a dry box containing silica gel with steady flow of purified dry nitrogen.

2. Rocks and other foreign material are removed from soil and crushed thoroughly by mortar and pestle.

3. Soil is weighed in extraction thimbles that have been previously extracted with diethyl ether under reflux. Soil is weighed on glassine paper and poured directly into extraction flasks if the shaker extraction technique is used.

4. Samples are extracted on Soxhlet apparatus for 8 hours, and the procedure is continued to Step 5 unless alternate shaker procedure is used.

In an attempt to shorten the time of extraction, a mechanical shaker was employed in the initial separation. In all cases the amount of organic residue extracted was greater by the Soxhlet method. This increased organic loading also puts a greater burden on the thin layer separation. Because of the many factors in the analysis, the Soxhlet method of extraction should be used for completeness of recovery when many varied soil sample types are being extracted. The mechanical shaker extraction may be employed when soil samples from the same area are being evaluated on a relative basis. The shaker extraction procedure utilized in this project is described in the following paragraphs.

Alternate Procedure for Shaker Extraction:

A. Place 50 g of soil in a 250 ml extraction flask with 60 ml benzene.

B. Shake for 1 hour and filter through glass wool into a 250-ml beaker.

C. Add 60 ml of benzene, shake for 30 minutes and filter as in "B."

D. Add 60 ml of benzene, shake for 15 minutes and filter as in "B."

E. Add 25 ml of benzene; hand shake for 2 minutes and filter; continue with the following Step 5.

5. Sample volumes are reduced in 250-ml beakers on a steam bath (to approximately 25 ml). The steam bath must be located in a hood.

6. Samples are filtered through sintered glass funnels into previously weighed test tubes.

7. Samples are dried in a vacuum oven at 60°C. Place each test tube in a beaker of water.

8. Any remaining moisture is removed by placing test tubes in a desiccator. Weigh test tubes to obtain extracted sample weight.

9. Prepare the Al_2O_3 thin layer plate as follows:

A. Remove 1/16 in. of alumina from each edge of the plate.

B. Scribe a small dot 1/4 in. from each edge and 7/8 in. from bottom.

C. Scribe a line across the plate 15 cm above these two dots.

D. Activate plate at 110°C for 1 hour.

10. Samples are dissolved in methylene chloride. 1.0 ml/25 mg of residue. Let the samples sit for a minimum of 15 minutes. Roll the tubes to get all of the sample from the sides.

11. One hundred ml of hexane is poured into tanks. Alternate tank solution: 20 ml benzene, 80 ml pentane.

12. The template is positioned over the glass plate so that the bottom edge casts a shadow connecting two previously scribed dots on plate. Pour sample into 5-ml beaker. Use thin-layer chromatography spotting capillaries, 5 µl, and condition before use by drawing 2 to 5 ml portions and emptying into a laboratory tissue. Spot 80 µl (or 40 µl) of methylene chloride solution of the extracts by placing a row of eight slightly overlapping spots on the

shadow line; then place an additional 5 µl on each spot (for 80 µl).

Standard solution of BaP:

10 mg of BaP

100 ml of methylene chloride.

Spot 2.0 µg of benzo[a]pyrene by applying 4- to 5-µl portions of BaP spotting standard in a close row. Allow at least 1 cm from sample.

13. The spotted plate is developed in the tank of hexane. Allow solvent to migrate to the 5-cm level. Dry in an oven at 70°C for 1 minute or until hexane is dry. Replace plate in tank and repeat process until the BaP appears to be separated when viewed with a hand-held UV light (> 350 nm). Dry the hexane and then allow the solvent to migrate to the 15-cm line. Remove the plate from the tank and place it under the UV light. Outline the separated benzo[a]-pyrene spot using the position and color of the standard as a guide. Then outline the spot containing the standard.

NOTE: When the plates were developed in benzene and pentane, they were allowed to sit in the humidity of the laboratory for 38 minutes (40 to 49 percent relative humidity) before they were positioned in the tank. The solvent migrated up to the 15-cm line in about 30 minutes.

14. Refer back to Step 9 of the initial procedure and complete the analysis.

RESULTS OF ANALYSES

Results of analyses of soil samples for their BaP content as extracted by both Soxhlet and shaker extraction procedures and analyzed via fluorescence emission at 540 nm are included in Table B-1.

DISCUSSION OF RESULTS

An Aminco-Bowman Scanning Fluorimeter was employed for all determinations. An excitation wavelength of 470 nm was used, and the linearity and response of the system was established over the concentration range in which the samples and standards were measured.

All solvents used were of the highest quality commercially available. New batches of solvent were checked for purity fluorometrically. The highest quality chemicals were purchased from commercial supply houses and their purity checked using thin-layer chromatography (TLC) and fluorescence. Pesticide Analysis Grade benzene was used exclusively as the extracting solvent.

Table B-1. RESULTS OF SAMPLE ANALYSIS FOR SOILS TAKEN IN WEST VIRGINIA (COAL REFUSE BANKS) AND IN CHARLESTON, S.C.

EPA sample	RTI sample no. (1372-124-)	Peak position			Concentration, µg/kg	Eluting solvent	Development	Method
		Sample	Standard	Δλ				
Cedar Grove, W. Va. (June 1, 1972)								
A-1-A	-1	525	540	15	1,004	Benzene/pentane(20/80)	Single	Soxhlet
	-1(2)	511	545	34	36	Benzene/pentane	Single	Shaker
A-2-A	-2	525	540	15	52	Benzene/pentane	Single	Soxhlet
	-2(2)	530	545	15	76	Benzene/pentane	Single	Shaker
A-3-A	-3	520	535	15	432	Benzene/pentane	Single	Soxhlet
	-3(2)	535	545	10	22	Benzene/pentane	Single	Shaker
A-4-A	-4	525	542	17	61	Benzene/pentane	Single	Soxhlet
	-4(2)	523	535	12	326	Benzene/pentane	Single	Shaker
Marnie, W. Va. (June 2, 1972)								
A-6	-5	510	535	25	32	Benzene/pentane	Single	Soxhlet
	-5(2)	520	535	15	513	Benzene/pentane	Single	Shaker
A-7	-6	532	542	10	1,475	Benzene/pentane	Single	Soxhlet
	-6(2)	528	545	17	904	Benzene/pentane	Single	Shaker
A-8	-7	543	543	0[a]	902	Benzene/pentane	Single	Soxhlet
	-7(2)	545	545	0[a]	712	Benzene/pentane	Single	Shaker
	-7A(1)[b]	543	543	0[a]	627	Benzene/pentane	Single	Soxhlet
	-7A(2)[b]	539	543	4[a]	969	Benzene/pentane	Single	Soxhlet
A-9	-8	544	544	0[a]	18,207	Benzene/pentane	Single	Soxhlet
	-8(2)	539	536	3[a]	10,132	Benzene/pentane	Single	Shaker
	-8(2)	543	543	0[a]	22,200	n-Hexane	Multiple	Shaker
	-8A[c]	542	542	0[a]	5,808	Benzene/pentane	Single	Soxhlet
	-8B(1)[d]	542	541	1[a]	10,800	Benzene/pentane	Single	Soxhlet
	-8B(2)[d]	542	541	1[a]	12.900	Benzene/pentane	Single	Soxhlet

Table B-1 (continued). RESULTS OF SAMPLE ANALYSIS FOR SOILS TAKEN IN WEST VIRGINIA (COAL REFUSE BANKS) AND IN CHARLESTON, S.C.

EPA sample	RTI sample no. (1372-124-)	Peak position			Concentration, µg/kg	Eluting solvent	Development	Method
		Sample	Standard	Δλ				
Cedar Grove, W. Va. (February 17, 1972)								
	-9	510	544	34	13,400	Benzene/pentane	Single	Shaker
	-9(2)	538	538	0[a]	1,050	Benzene/pentane	Single	Shaker
	-9(2)A[e] Sea sand with BaP	524	542	18	1,690	Benzene/pentane	Single	Shaker
	-10	538	542	4[a]	2[f]	Benzene/pentane	Single	Soxhlet
	-10(2)	520	538	0	179	Benzene/pentane	Single	Shaker
Charleston, S.C.								
C-19-A-B	-11	530	544	14	33	Benzene/pentane	Single	Shaker
	-11(2)	519	541	22	216	n-Hexane	Multiple	Soxhlet
C-19-C1-B	-12	530	544	14	529	Benzene/pentane	Single	Shaker
	-12A	523	541	18	326	Benzene/pentane	Single	Shaker
	-12(2)	521	541	20	1,920	n-Hexane	Multiple	Soxhlet
C-17-B	-13	505	544	39	71	Benzene/pentane	Single	Shaker
	-13(2)	519	541	22	196	n-Hexane	Multiple	Soxhlet
C-24-A	-14	515	545	30	63	Benzene/pentane	Single	Shaker
	-14(2)	518	539	21	696	n-Hexane	Multiple	Soxhlet
C-25-C	-15	541	545	4[a]	107	Benzene/pentane	Single	Soxhlet
	-15(2)	518	539	21	1,003	n-Hexane	Multiple	Shaker
C-26A-B	-16	522	542	20	3,634	Benzene/pentane	Single	Shaker
	-16A[e]	520	543	23	1,530	n-Hexane	Multiple	Shaker
	-16(2)	516	539	23	247	n-Hexane	Multiple	Soxhlet
C-31A	-17	522	542	20	209	Benzene/pentane	Single	Shaker
	-17(2)	522	540	18	606	n-Hexane	Multiple	Soxhlet

Table B-1 (continued). RESULTS OF SAMPLE ANALYSIS FOR SOILS TAKEN IN WEST VIRGINIA (COAL REFUSE BANKS) AND IN CHARLESTON, S.C.

EPA sample	RTI sample no. (1374-124)	Peak position			Concentration, µg/kg	Eluting solvent	Development	Method
		Sample	Standard	Δλ				
Charleston, S.C.								
C-38A-B	-18	524	542	18[b]	823	Benzene/pentane	Single	Shaker
	-18(2)	523	540	17	2,502	n-Hexane	Multiple	Soxhlet
C-39A-1-B	-19	539	539	0[a]	953	Benzene/pentane	Single	Shaker
	-19(2)	539	540	1[a]	829	n-Hexane	Multiple	Soxhlet
C-39A-2-B	-20	543	540	3[a]	97,612	Benzene/pentane	Single	Shaker
	-20A[e]	539	542	3[a]	64,600	Benzene/pentane	Single	Shaker
C-39A-3-B	-21	530	542	12	1,875	n-Hexane	Multiple	Soxhlet
C-39B-B	-22	522	542	20	150	n-Hexane	Multiple	Soxhlet
C-45-B	-23	521	542	21	1,095	n-Hexane	Multiple	Soxhlet
C-46D-B	-24	541	541	0[a]	33,528	n-Hexane	Multiple	Soxhlet
C-47-D-B	-25	521	541	20	489	n-Hexane	Multiple	Soxhlet
C-52-B	-26	542	541	1[a]	27,709	n-Hexane	Multiple	Soxhlet
C-52C-B	-27	522	542	20	231	n-Hexane	Multiple	Soxhlet
C-53B-B	-28	543	542	1[a]	3,520	n-Hexane	Multiple	Soxhlet
C-62A-B	-29	519	542	23	255	n-Hexane	Multiple	Soxhlet
NSC-1773	-30	523	544	21	178	n-Hexane	Multiple	Soxhlet
26C-B	-31	523	544	21	206	n-Hexane	Multiple	Soxhlet
27C(CHK-39A2)-1B	-32	536	544	18	827	n-Hexane	Multiple	Soxhlet
-2B	-33	531	542	11	1,518	n-Hexane	Multiple	Soxhlet
-3B	-34	531	542	11	809	n-Hexane	Multiple	Soxhlet
-4B	-35	539	542	3[a]	2,354	n-Hexane	Multiple	Soxhlet
-5B	-36	530	544	14	7,087	n-Hexane	Multiple	Soxhlet
-6B	-37	525	544	19	1,920	n-Hexane	Multiple	Soxhlet
28C-37A	-38	524	544	20	3,099	n-Hexane	Multiple	Soxhlet

Table B-1 (continued). RESULTS OF SAMPLE ANALYSIS FOR SOILS TAKEN IN WEST VIRGINIA (COAL REFUSE BANKS) AND IN CHARLESTON, S.C.

EPA sample	RTI sample no. (1374-124-)	Peak position			Concentration, µg/kg	Eluting solvent	Development	Method
		Sample	Standard	Δλ				
Charleston, S.C.								
30C-43B	-39	522	537	15	500	n-Hexane	Multiple	Soxhlet
32-C(48-0)	-40	523	537	14	912	n-Hexane	Multiple	Soxhlet
33-C(49-B)	-41	523	537	14	982	n-Hexane	Multiple	Soxhlet
C-36 39B	-42	525	537	12	910	n-Hexane	Multiple	Soxhlet
C-38 25A	-43	523	537	14	944	n-Hexane	Multiple	Soxhlet
C-39 110-A	-44	525	537	12	1,408	n-Hexane	Multiple	Soxhlet
C-39 110-B	-45	524	540	16	1,807	n-Hexane	Multiple	Soxhlet
C-40-46A-B	-46	523	540	17	2,595	n-Hexane	Multiple	Soxhlet
C-43,2A	-47	522	540	18	5,489	n-Hexane	Multiple	Soxhlet
C-49,67A	-48	521	544	23	201	n-Hexane	Multiple	Soxhlet
C-47,16A	-49	521	544	25	378	n-Hexane	Multiple	Soxhlet

[a]Peak comparison ≤ 4 nm.

[b]Second spotting, both from methylene chloride sample of Soxhlet extract and spotted on same plate with two standards.

[c]Second spotting, both from methylene chloride sample of Soxhlet extract.

[d]Third spotting, both from methylene chloride sample of Soxhlet extract spotted on same plate with two standards.

[e]Second spotting from methylene chloride sample of mechanical shaker.

[f]1.04 µg added.

[g]2.0 µg added, read at 538.

Results indicate that the optimum TLC solvent system of n-hexane is preferred over the 20/80 benzene-pentane mixture. Multi-development was required over 95 percent of the samples analyzed. The use of a scanning versus a filter fluorimeter is required because of the large number of interfering species that must be overcome in the separation. The scanning fluorimeter allows one to compare the fluorescence emission curves of the BaP standard and sample, which were separated in situ from the Al_2O_3 plate. The excitation wavelength can also be varied in an attempt to resolve the fluorescence emission spectra. In the cases in which the fluorescence emission of the sample differed more than 4 nanometers, the concentration of the sample was calculated on the basis of the relative fluorescence emission at the wavelength of the standard separated from the aluminum oxide plate; consequently, the results reported in these cases can be compared to other results in which only a filter fluorimeter is used.

The fluorescence method for B in soil requires an involved separation by thin layer chromatography. A poor separation or inaccurate marking of the BaP from the organic constituents on the thin layer plate will usually produce very high results.

RECOMMENDATIONS

1. The analysis of soil samples for BaP should be done with a scanning spectrofluorimeter. A TLC scanner affixed to the spectrofluorimeter would permit location of the desired spot on the thin layer plate and quantitation without removal of the substrate from the plate.

2. Following extraction and evaporation of solvent, the residue should be dissolved in an organic solvent such as pentane and extracted with a dilute acidic solvent to remove basic organic interferences.

3. An extensive evaluation of the TLC system should be undertaken to determine the optimum solvent system and adsorbent. The matrices of various soil samples are quite different.

4. Further investigation should be devoted to development of a high-speed liquid chromatographic procedure for separation and detection of BaP.